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**PROGRAM**  
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**ABSTRACTS**

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Interdisciplinary Conference on

**ELECTRIFIED  
INTERFACES**

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*ONR*

September 16 - 21, 1990  
Asilomar, California

**91-12193**



**Interdisciplinary Conference on Electrified Interfaces**  
**Asilomar, California**

The past decade has seen a renaissance in the field of interfacial electrochemistry. There are at least three reasons for this growth in interest. Firstly, there has been a general recognition of the importance of interfacial science, resulting in part from the development of thin film technologies and the resultant heightened awareness of corrosion problems. Secondly, there have been theoretical advances which give promise of insights and predictions. Thirdly, there is the development of new techniques capable of probing the interface on a molecular level. In the near future, these may be able to provide experimental tests of the new theoretical insights.

New developments in such technologically important areas as energy conversion (fuel cells), energy storage (batteries) corrosion, and electrosorption (miniaturization of circuitry) are likely to hinge on a detailed, microscopic understanding of the electrochemical interface and processes which occur there. Superior basic research, which is stimulated by the free and open exchange at meetings, is essential to the development of these (or any) technologies.

In view of the importance of this subject, a meeting was held in Asilomar, Monterey, California, September 16-20, 1990. It brought together a group of scientists interested in theoretical and experimental problems related to nontraditional methods in interfacial electrochemistry, from both fundamental and applied points of view. This was a continuation of the successful biannual series of meetings which began in Snowmass, Colorado in 1979 and was continued in Logan, Utah, Telavi, USSR, Berlin, FRG and in Bologna, Italy. This series of meetings differs from the conventional meetings in this country because of its unique focus on the physical aspects of electrochemistry. In addition, this series of meetings attracts investigators from other disciplines who have nontraditional and often stimulating approaches to interfacial problems. Approximately one hundred attendees from North America, Europe, and New Zealand participated in discussions related to the most recent advances in the subject area.

### **Conference Program**

Twenty one reviews of forty minutes duration were presented. Each presentation was followed by twenty minutes of lively discussion. The reviews were divided into four subject areas:

1. Theory and structure
2. Overlapping double layers and colloids
3. Redox and interfacial electron transfer
4. Experimental characterization

This conference was the first in this series in which overlapping double layers and colloids was represented. Following the presentations for each subject area there was a poster session which consisted of viewing followed by discussion, lead by a panel of three experts. There were approximately seventy posters presented. A copy of the program and poster abstracts is attached as Appendix I. A list of participants is attached as Appendix II.

Sunday evening was devoted to a discussion lead by Doug Bennion, on the current status of cold fusion. The conclusion was that the calorimetric measurements are difficult and not a reliable indicator of cold fusion but there was a growing body of nuclear measurements which were consistent with a low level of cold fusion occurring in these systems. The general consensus was that there are a number of observed anomalies which are not well understood and that most experimental efforts should be put into the correlation of simultaneous events, i.e. measurements of excess heat occurring at the same time as nuclear events.

The stage for the rest of the conference was set on Monday morning by Sergio Trasatti, who reviewed the correlation of metal properties with electrochemical phenomena. The theoretical inter-

pretation of Trasatti's data is fairly well understood for the sp metals but poorly understood for sd metals, such as gold and silver. Schmickler discussed the theory of the specific adsorption of anions on metal surfaces. Bagus reported on cluster model studies of surface adsorbates interactions and the effect of electric field, and Peter Rossky reviewed calculations of the structure of water at interfaces. Glen Torrie discussed his own work using the hypernetted chain approximation with a quadropolar model of water, where he finds extensive structuring at the interface.

The second day was devoted to overlapping double layers, colloids, membranes and related topics. Bo Jonsson reported that he has observed an electrostatic attraction between like charged plates due to correlations within the ionic fluid between plates. This new phenomena has yet to be observed experimentally. Mike Klein reported on his simulations of micellar systems. His talk illustrated the utility of simulations and graphics. Evan Evans gave a presentation of the effect of long range effects on capillary forces, waves and thermodynamics of deformable membranes. Marc Anderson reviewed several applications of cylindrical internal reflection FTIR for in-situ surface chemical studies of colloidal  $\text{-FeOOH}$  (goethite). Hangelein discussed the dependence of the photochemical properties of colloidal metal and semiconductor particles on their size and bulk properties.

In the area of redox and interfacial electrochemistry, H. Kim explained the latest advances in the theory of electron transfer in which nonlinear quantum effects are included. Marshall Newton outlined his latest work on theory of electron transfer and indicated the role of the solvent in the electron. The final theoretical talk was that of Ron Fawcett who discussed the kinetics of amalgam formation in nonaqueous solvents. Ulrich Stimming reported on recent results using frozen electrolyte electrochemistry techniques. These techniques greatly expand the temperature range for which transport and electron transfer studies can be made. Joe Hupp showed experimentally that a time dependent analysis of resonance-enhanced Raman scattering can lead to a complete mode-by-mode description of the vibrational structural changes accompanying charge transfer.

The last sessions were devoted to new experimental methods for characterizing the electrochemical interface. John Porter described a technique for measuring the force between adjacent mercury droplets in aqueous solutions. From this the structure of water in the double layer can be inferred. Joe Gordon reviewed recent advances in structural studies of adlayers at well defined surfaces using x-ray techniques. Bruno Pettinger discussed recent advances and vibrational spectroscopy and second harmonic generation studies at electrified interfaces. The final two talks presented by Bruce Schardt and Jurgen Behm were devoted to perhaps the most exciting new experimental technique in electrochemistry, namely STM. Both speakers were able to obtain atomic resolution of electrochemical surfaces.

## CONCLUSIONS AND RECOMMENDATIONS

From the discussion of the paper and posters at this meeting it is apparent that there has been a revolution in experimental techniques. Through a variety of techniques it is now possible to obtain structural information of electrochemical interfaces with atomic resolution. There has been a similar advance in the application of statistical mechanical theories of fluids to the interface which has lead to calculations incorporating molecular models of water. One of the benefits of this series of meetings has been to bring together theorists and experimentalists. When this series began in Snowmass a decade ago it was evident that theorists and experimentalists were largely decoupled. They worked on different problems and spoke different languages. This has changed dramatically. One can almost see the convergence of theory and experiment.

The key challenges for the immediate future in theory are to incorporate more realistic molecular models of water and to include discrete models of the electrode surface. For experimentalists it was time to move from characterization of adsorbates to probing the structure of the liquid side of the interface. The theory and experiment of colloidal systems will aid in the realization of these goals because the force between colloidal particles is not an integrated quantity, as are many conventional

electrochemical quantities, and so provides direct information about interfaced fluid structure, especially water. Coupled with advances in our understanding of the electron transfer process, a true understanding of the electrochemical interface and processes which occur, they may be realizable in the foreseeable future.

As a result of the general level of excitement which this meeting created, future meetings are planned in Oxford in 1992 and in France in 1994.

**Interdisciplinary Conference on Electrified Interfaces**  
**Asilomar, California**

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## PROGRAM

### SUNDAY EVENING —

#### Roundtable Discussion on Cold Fusion

E. YEAGER — Program Chairman, *Case Western Reserve University, Cleveland, OH*  
 M. FLEISCHMANN, *University of Southampton, U.K.*  
 D. BENNION, *Brigham Young University, Provo, UT*  
 M. FOWLER, *Los Alamos National Laboratory, Los Alamos, NM*

### LECTURES & SPEAKERS

#### (1) Theory and Structure of Electrified Interfaces — Session A

Monday Morning — 9:00-12:00

- New Experimental Data for Theory  
(S. TRASATTI, *University of Milan, Italy*)
- Specific Adsorption  
(W. SCHMICKLER, *University of Bonn, FRG*)
- The Effect of Electric Fields on the Surface-Adsorbate Interaction  
(P. S. BAGUS, *IBM Research, San Jose, CA*)

#### (1) Theory and Structure of Electrified Interfaces — Session B

Monday Evening — 7:00-10:00

- Structure of Water at Interfaces  
(P. ROSSKY, *University of Texas, Austin, TX*)
- Integral Equation Studies of Electrolyte Solutions at Charged Surfaces  
(G. TORRIE, *Royal Military College, Kingston, Canada*)
- Poster Discussion

#### (2) Overlapping Double Layers, Colloids, Bilayers and Related Topics — Session A

Tuesday Morning — 9:00-12:00

- Monte Carlo and Mean Field Calculations of Forces Between Colloidal Particles  
(B. JÖNSSON, *University of Lund, Sweden*)
- Molecular Dynamics Studies of Amphiphilic Assemblies  
(M. KLEIN, *University of Pennsylvania, Philadelphia, PA*)
- Thermal Fluctuations of Electric Double Interactions Between Bilayer Membranes  
(E. EVANS, *University of B.C., Vancouver, Canada*)

#### (2) Overlapping Double Layers, Colloids, Bilayers and Related Topics — Session B

Tuesday Evening — 7:00-10:00

- ATR-FTIR and Raman Spectroscopy at Hydrous Oxides and Ceramic Membranes  
(M. ANDERSON, *University of Wisconsin, Madison, WI*)
- Optical and Photochemical Properties of Colloidal Metal and Semiconductor Particles  
(A. HENGLEIN, *Hahn-Meitner Inst., Berlin, W. Germany*)

**(3) Redox and Interfacial  
Electron Transfer — Session A**

**Wednesday Morning — 9:00-12:00**

- Electron Transfer Reactions at Electrodes  
(J. T. HYNES, *University of Colorado, Boulder, CO*)
- Electronic Structural Control of Electron Transfer Kinetics  
(M. NEWTON, *Brookhaven National Laboratory, Upton, NY*)
- Role of the Solvent in Electron and Ion Transfer Reactions  
(W.R. FAWCETT, *University of California, Davis, CA*)

**(3) Redox and Interfacial  
Electron Transfer — Session B**

**Thursday Morning — 9:00-12:00**

- Frozen Electrolyte Studies  
(U. STIMMING, *Columbia University, NY*)
- Surface Intervalence Enhanced Raman Scattering  
(J. HUPP, *Northwestern University, Evanston, IL*)
- Poster Discussion

**(4) Experimental Characterization  
of the Electrified Interface —  
Session A**

**Thursday Evening — 7:00-10:00**

- Study of Metal/Liquid Interfaces with Tunnel Junction Devices  
(J. PORTER, *University of California, Berkeley, CA*)
- Structure of Metal Adlayers on Ag(111)  
(J. G. GORDON, *IBM Research, San Jose, CA*)
- In-Situ Raman and SHG Studies  
(B. PETTINGER, *Fritz-Haber Instiut, Berlin, FRG*)

**(4) Experimental Characterization  
of the Electrified Interface —  
Session B**

**Friday Morning — 9:00-12:00**

- Examination of Adsorbates on Electrodes Using STM  
(B. SCHARDT, *Purdue University, West Lafayette, IN*)
- Structure of Underdeposited Metal Adlayers Observed by STM  
(J. BEHM, *Instiut für Physikalische Chemie-Munchen, FRG*)
- Poster Discussion

\* \* \*

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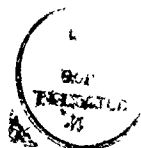
## FT-RAMAN SPECTRA AND THE STRUCTURE OF ADSORBED 2,2'-CYANINE

D. L. Akins, J. W. Macklin and H.-R. Zhu, The City College of The City  
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### ABSTRACT

Near infrared excited FT-Raman spectra of 2,2'-cyanine adsorbed onto a smooth silver electrode and of polycrystalline 2,2'-cyanine are compared with dispersive Raman spectra obtained using visible excitation to determine adsorbate structural characteristics. Raman spectra are interpreted as indicating that 2,2'-cyanine exists as a structural composite of polycrystalline and two intermolecular arrangements of cyanine monomers forming the J-aggregate. This structural model is shown to explain Raman intensity variations that depend upon dye concentration, supporting electrolyte, pH, and electrode potential. Variations of the FT-Raman relative band intensities over a surface potential range in which the surface concentration increases indicate that one of the structural conformers in the J-aggregate is thermodynamically favored at more negative potentials.

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USE OF ATR-FTIR AND RAMAN SPECTROSCOPY  
IN AQUEOUS INTERFACIAL STUDIES INVOLVING HYDROUS OXIDES AND CERAMIC MEMBRANES

Lane Tiekkanen  
M. Isabel Tejedor-Tejedor  
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Cylindrical Internal Reflection Fourier Transform Infrared Spectroscopy (CIR-FTIR) is a type of ATR spectroscopy which can not only be applied to aqueous solutions but can as well be applied to studies of colloidal suspensions. We have been employing this technique to study the interfacial chemistry between an aqueous solution and a hydrous oxide surface. In this talk we present a brief review on the methodology of the technique in aqueous suspensions of colloidal particles, some of the quantitative aspects of the technique and some of the applications of the technique to the qualitative understanding of the interfacial chemistry of these systems.

Time permitting, we will also discuss the applications of ATR-FTIR as well as Raman wave guide spectroscopy to interfacial studies involving ceramic membranes. These interesting new materials are nano-porous materials which are comprised of very small oxide particles. Since these membranes have a high degree of surface area, they act as effective adsorbents and greatly increase the signal to noise ratio in Raman studies. In addition, they can be fashioned into porous electrodes and photoelectrodes for the spectroscopic examination of electrochemical and photoelectrochemical processes.

\* Person Presenting the Talk

# INFRARED SPECTROSCOPY TO PROBE THE ELECTROCHEMICAL DOUBLE LAYER

Kevin Ashley and Frederick Weinert

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## ABSTRACT

The infrared spectra of molecules and ions which are specifically adsorbed to the electrode surface can be used to probe the dynamics and structure of the interfacial region. In this work the infrared spectra of adsorbed cyanide and thiocyanate species are obtained in the electrical double layer potential region. In turn, the potential dependent behaviors of the infrared spectra of these ions are monitored as certain experimental variables are altered. Theoretical calculations from model cyanide and thiocyanate adsorbates are used to compare the predicted infrared frequencies of the surface species with the observed experimental infrared spectroelectrochemical frequencies. The effects of an externally applied field on the infrared frequencies of the adsorbed ions are modelled theoretically using a semiempirical approach. Also, this semiempirical theoretical method is employed in an effort to account for differences in infrared frequencies observed for similar adsorbates on different electrode surfaces. In this way it is possible to examine changes in adsorbate bonding characteristics by modelling the observed surface infrared spectra of specifically adsorbed species. Examples are presented for cyanide adsorbed on platinum and palladium, and thiocyanate adsorbed on platinum, gold, and silver.

# THE MERCURY / NON-AQUEOUS SOLVENT INTERFACE

## A NEW ANALYSIS OF CAPACITANCE DATA

S. Amokrane and J.P. Badiali

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The theoretical analysis of capacitance data at the ideally polarized interface in absence of ionic specific adsorption includes now the contribution of the metal and that of the metal-solvent coupling. The first step in this direction was the introduction in the models of a description of the metal surface in which the metal does not behave like an ideal conductor. Later it was recognized that for a weak metal-solvent coupling, the distance of closest approach of the solvent molecules to the surface of the electrode should depend on the strength of the interfacial electrical field. These two effects lead to a contribution  $C_m$  to the inner layer capacitance  $C_i$ . We have shown that  $C_m$  which results from general phenomena is, to a large extent, independent of the remaining contribution  $C_s$  to  $C_i$ . Thus  $C_s$  defined by  $1/C_s = 1/C_i - 1/C_m$  represents a semi-empirical determination of the real contribution of the solvent to the capacitance. This new analysis of the capacitance has been applied to various metal/ aqueous solutions interfaces and the effect of the temperature has been investigated [1].

This work represents an extension of this analysis to the case of eight non-aqueous solvents. It is found that in almost all cases the solvent contribution  $C_s$  has a common general behaviour with the charge  $q_m$ .  $C_s(q_m)$  is simply a bell shaped curve. The solvent specificity determines the magnitude of  $C_s$  and the charge  $q_{max}$  at which the maximum of the  $C_s(q_m)$  curve occurs. This suggests that the classification of different solvents according to the shape of the  $C_i(q_m)$  curves might not be appropriate. After separation from  $C_s$  of a contribution  $K_{ion}$  due to free charges and rescaling the charge on the electrode into  $q_m - q_{max}$ , definitive correlations are inferred concerning the capacitance  $C_s(dip)$  associated to the orientation of permanent dipoles. Since the range of variation of  $C_s(dip)$  is strikingly smaller than that of  $C_s$  we conclude that the molecular size is the dominant factor which determines the magnitude of  $C_s$  around  $q_{max}$ . Near  $q_{max}$ , the small remaining variations observed in the  $C_s(dip)$  curves is found to depend on the nature of intermolecular interactions in the solvent layer. At moderate charges, the results for aprotic solvents almost merge into a single curve while those corresponding to associated solvents are separated. At high values of  $q_m$  the rate at which saturation of the polarization appears depends on the chemical nature of the solvent.

In conclusion, the behaviour of different inner layer  $C_i$  curves is determined to a large part by common physical phenomena. The  $C_s(q_m)$  curves are specific to each solvent and intermolecular interactions determines the behaviour of  $C_s(dip)$ .

# STRUCTURE OF THE PASSIVE LAYER ON A LITHIUM ANODE.

## A SIMPLE THEORETICAL APPROACH.

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When a surface of lithium is put in contact with an organic solvent, a passive layer is created. This layer can be studied by considering different length scales. Here, we focus on the structure of the overall layer which can reach 1 micrometer or more than thousand times the usual order of magnitude of any molecular diameter. At this scale the structure of the layer can be described in terms of macroscopic quantities. Besides these physical parameters which depend on the chemical nature of the material formed on the anode, we introduce some geometrical parameters which characterize the structure of the layer. Here we assume that the material is aggregated in small cylinders defined by their radius and their volume. For a given configuration of the layer we determine the part of the free energy which depends on the geometry. The minimization of the free energy allows us to calculate the influence of the physical parameters on the structure.

The free energy contains three terms. One characterizes the free energy of one cylinder in presence of the solvent. This term includes the interfacial tension between a cylinder and the solvent and a curvature energy related to the finite dimension of the cylinder. The second term takes into account the interaction between cylinders. It contains an attractive part related to the dispersion interaction and a repulsive one determined by the solvation energy, the coupling between double layers, ... . The last part of the free energy introduces the entropy of the system which is estimated via a Flory-Higgins approach.

We show that the model can generate various kinds of structure: cylinders isolated in a solvent or conversely some channels of solvent crossing a piece of compact solid, or even more generally an entangled structure. Quantitatively, the structure is characterized by the radius of the cylinder and a more global quantity as the porosity or the swelling of the layer. The structure of the layer is also discussed in relation with the percolation phenomenon.

In such a difficult domain the main task of the theory is not to predict some precise experimental facts for which, in addition, the reliability is not so high but to discover what are the physical ingredients which can lead to various morphologies. Although the theory is in its first stage of development, it is used for analyzing some experiments in which the structure of the passive layer is qualitatively different ( compact solid, porous material or polymeric structure).



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The significance of studies on science and technology of transition metal chalcogenides ( $MCh_n$ ), particularly dichalcogenides, transition metal oxy-halides (MOX), and transition metal oxides ( $MO_n$ ), is based on their abundance in nature as well as their interesting physico-chemical properties. Besides the utilization of such chemicals and of their intercalation products as the electrode materials in high energy density aqueous and non-aqueous lithium batteries, solar cells and other physicochemical energy conversion and storage devices, studying the detail of their preparative procedures, characterization methodologies, together with the kinetics and mechanism of the charge transfer induced interfacial processes in homo- and heterogeneous catalysis seems crucial.

Chalcogenides with chain- or layer-like frameworks may in certain circumstances approximate to one or two dimensional structures. However, they exhibit a number of properties which lie between the one and three dimensional types of solids. Quasi one dimensional  $MCh_3$  materials are keenly interesting due to their peculiar transport properties. The  $MCh_2$  substances show a nice variety of geometric and electronic situations, namely they exhibit highly anisotropic physical properties and various charge density wave, CDW, (related to the two dimensional character of the Fermi surfaces) and the superconducting phase transitions. The structure of CDW states depend on the crystal structure. In  $MCh_2$  materials the d-CB and the generally strong electron-phonon coupling provides the bases for superconductivity. In other words, it is shown that there are two factors responsible for the superconductivity of the materials: (i) the dynamic effect of the attraction of the similarly charged particles inducing their coupling, (ii) the zero spin of pairs as Bose- particles. By considering the kinetics and mechanism of intercalation reactions as well as the structure and dynamics of the acquired products, there are three types of phase transitions observed in  $MCh_2$  intercalation systems with regard to: (i) the host structure through a shifting of its slabs, (ii) an occupancy of different sites by the guest ions and molecules (or atoms) and (iii) electronic transitions induced by the electron transfer processes. Moreover, two dimensional (or single layer) superconduction has always been an intriguing experimental possibility in layered structure materials. Intercalation chemistry appears as a competition between a cost in strain energy needed for example to open the Van der Waals gap of two dimensional structures and a gain in electronic energy. Another noteworthy factor is the configurational entropy of the intercalated species.

It should be added that not only understanding the physics and chemistry of the  $MCh_n$  materials but a rather broad class of lamellar compounds will permit deep understanding of the kinetics, mechanism, structure and dynamics of the host and guest in the course of intercalation and photointercalation reactions and the products as well. Since accurate knowledge about the electron transfer processes (on the basis of the theory of Mulliken-Dogonadze-Gerischer-Marcus, MIDGM) in such reactions play significant roles in analyzing the electrode reactions, the design of new materials and reactors bring about many possibilities to obtain particular catalytic media for use in advanced energy conversion and storage devices. The MOX compounds, e.g.  $FeOCl$ , with a bi-dimensional structure, function as the host for a variety of intercalation reactions being of practical significance in technology such as in lithium batteries, etc. The following reaction holds for  $x \geq 1$ , and

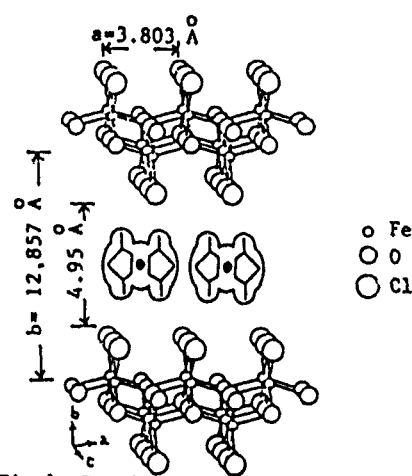
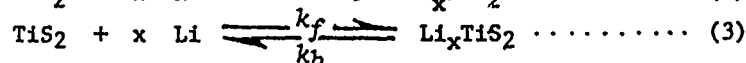


Fig.1, Topological representation of of intercalation of cobaltocene into  $FeOCl$ . The structural parameters:  $a = 3.803$ ,  $b = 25.698$ ,  $c = 3.335$  for the layer expansion  $4.94 \text{ Å}^0$ .

a sharp semiconductor to metal transition occurs as the consequences of electron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at the percolation threshold in  $\text{Li}_x\text{FeOCl}$ . Reaction (1) proceeds reversibly for the cathodic potential and corresponds to a current flow between the working and counter electrodes. On the basis of similarities between the guest diffusion processes as well as the reversible alkali metal chemical and electrochemical intercalation reactions of the MOX and  $\text{MCh}_2$  made clear the resemblance of the reactions (1) to (3):



Studies on photoelectrochemical behaviors of  $\text{MCh}_2$  layered materials necessitates consideration of the strongly asymmetric surface properties of the perpendicular,  $\text{C}_\perp$ , (VdW surface) and parallel,  $\text{C}_\parallel$ , (R surface) at the interfaces. Thus in analogy with chemical and electrochemical intercalation reactions, photoinduced intercalation process for some semiconductive electrodes seems feasible.

(For a short biography please refer to: IUPAC, *Chem.Intl.* 10(3,5), 85, 170 (1988)). Ref. S. K. Bahador, in "Hydrogen absorbing materials/Catalytic materials", p. 215, MRS-IMAM 2, MRS, Pittsburgh, 1989.

THE ELECTRIC DOUBLE LAYER AROUND AN ISOLATED  
SPHERICAL MACROION<sup>+</sup>

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The Modified Poisson-Boltzmann (MPB) equation is used to study the ionic distribution in the neighbourhood of an isolated spherical macroion. The electrolyte surrounding the colloid particle is represented by the restricted primitive model. The MPB equation is formulated for this model and solved numerically using a quasi-linearization technique. Comparisons are made with the Poisson-Boltzmann and the HNC/MSA theories for 1:1 and 2:2 electrolytes for various values of the colloid charge or potential, the colloid radius and the electrolyte concentration.

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# Counterion Binding in the Solvation Shell of Ionized Micelles in Aqueous Solution

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Diffraction results for the structure of micellar colloids are often interpreted on the basis of the primitive model for ionic solution. In this model, the ions and polyions are pictured as charged hard spheres in dielectric continuum. The binding of the counterions to the micelles deduced from the measurements is, however, usually stronger than is predicted by the above model. In the present work, an additional contribution to the polyion-counterion association related to the reduced permittivity in the solvent layer adjacent to the micelle is estimated. The spatial correlations in the solution are studied using the Ornstein-Zernike/Hypernetted Chain approximation. The enhanced ion-micelle attraction gives rise to stronger screening of the Coulombic repulsion among the micelles. The reduced order in the solution conforms with the experimental observations. In extreme cases, a partial association of the micelles linked by the common counterions is observed.

# **Phase Transition of Quasi Two Dimensional Water Between Conducting Surfaces**

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## **ABSTRACT**

The effect of an external DC electric field in water between two conducting surfaces has been studied at the temperature of 300K by molecular dynamics. We present a new structure of water layers and the evidence for the existence of the continuous phase transition induced by the external field. The phase transition occurs at the maximum of entropy as a function of the external field, which is consistent with a previous experimental observation. Use of the classical response theory allows a Landau type analysis of the phase transition. The results show the possible field dependent structure of the Helmholtz double layer.

# STUDIES OF ELECTROACTIVE MONOLAYERS SELF-ASSEMBLED ON AU ELECTRODES

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## ABSTRACT

Molecules with an electroactive group inserted into an alkyl chain with sulfide functionality were synthesized to study electron transfer from an electrode through a non-conjugated hydrocarbon spacer. The molecules were self-assembled with octadecylmercaptan onto Au electrodes. The sulfide binds to the gold and the hydrocarbon chains orient more nearly perpendicular than parallel to the surface. The results of studies using cyclic voltammetry, FTIR, surface Raman spectroscopy and ellipsometry are reported. Electron transfer depended on the distance of the electroactive group from the surface, but was facile even at distances of up to 12 Å.

## ELECTROCHEMICAL PROPERTIES OF SURFACE MODIFIED SPRAYED $\text{SnO}_2$ FILMS

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Transparent and highly conductive  $\text{SnO}_2$  films are interesting to be used as counter-electrodes in photoelectrochemical (PEC) devices. But it is well recognized that  $\text{SnO}_2$  films in contact with a redox electrolyte present the disadvantage of a low transfer kinetics. This poor electrochemical response severely limits the overall performances of PEC cells. It has been previously shown that interfacial charge transfer could be significantly improved by metal deposition (for instance, Ir, Pt, Pd ...) rather than by bulk incorporation of deposits. To achieve such a surface modification, we have developed two approaches : (i) radiolytic grafting of metal nanoaggregates by  $\gamma$  irradiation [1] ; (ii) metal photodeposition with UV illumination under open circuit conditions [2]. Both techniques lead to the formation of small-sized islands (between 2 and 100 nm) with a surface density in the range  $10^8 - 10^{13} \text{ cm}^{-2}$ . Optical transparency remains unchanged when limiting the amount of deposited metal around  $10^{16} \text{ atoms/cm}^2$ . Our results for various redox systems ( $\text{Fe}(\text{CN})_6^{3-/4-}$ ,  $\text{I}_2/\text{I}^-$  ...) show that such discontinuous metal deposits strongly improve transfer kinetics.

Capacitance measurements prove that even highly conductive  $\text{SnO}_2$  behaves like a semiconducting material. A space charge layer exists which gives rise to a potential drop in  $\text{SnO}_2$ . Charge transfer occurs by tunnelling through a barrier depending on the distance between the bottom of the conduction band and the redox level. It is additionally controlled by the small number of states available at the bare  $\text{SnO}_2$  surface. Exchange currents are low and the cathodic and anodic branches of I-V curves are dissymmetric.

Electrochemical characterizations show that after surface-modification highly conductive  $\text{SnO}_2$  behaves like a massive metallic electrode. The first reason to explain this result is that band-bending inside  $\text{SnO}_2$  is fixed, only depending on the work function of the metal aggregates (determined by photoemission spectroscopy). As a consequence, the overpotential is now fully applied at the metal-solution interface. The second reason is that the tunnelling process inside  $\text{SnO}_2$  is made easier because of the high density of interface states created by the metal deposition.

Examples of application will be presented concerning the PEC response of Si photoelectrodes covered by a sprayed  $\text{SnO}_2$  thin films with and without surface modification.

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# EFFECT OF THE IONIC STRENGTH OF THE SUPPORTING ELECTROLYTE ON THE KINETICS OF ALBUMIN ADSORPTION AT A GLASSY CARBON ROTATING DISK ELECTRODE.

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The effect of ionic strength of the supporting electrolyte ( phosphate buffer, pH =7.4,  $xM + 10^{-2}x Fe(CN)_6K_4$ ,  $25^{\circ}C$ ,  $10^{-2}M \leq x \leq 1M$ ) on the kinetics of the adsorption of bovine serum albumin at a glassy carbon rotating disk electrode (RDE) was investigated. The RDE was mirror polished ( $1\mu m$  abrasive alumina) and polarised at -670 mV / SCE. This value corresponds to an electrical charge of the interface of ca.  $-10 \mu Cb.cm^{-2}$ , for  $x = 0.1M$ . The kinetics were determined by analyzing the double layer capacitance  $C_d(t)$  variation during adsorption [1, 2]. The experimental variation obeys the following relationship:  $C_d(t) = a_0 + \sum_i a_i \exp(-t / \tau_i)$  (1), the number  $i$  of detectable exponential functions depending on ionic strength. The time constants  $\tau_i$  are related to the kinetic parameters of the successive irreversible steps of the mechanism, and  $a_0$ ,  $a_i$  to the double layer capacitance for the various states of the interface (bare or entirely covered by the adsorbed protein in state  $i$ ). All the parameters involved in eq.(1) depend on the ionic strength. For  $x \geq 0.1M$ ,  $C_d(t)$  is monotonic and only two steps are required in the mechanism to account for the variation, whereas for  $x < 0.1M$ ,  $C_d(t)$  is non-monotonic and four steps are required. The various effects are explained by two main reasons which pre-exist in the absence of adsorption, i.e i) a change of the properties of the interface with the ionic strength (change of electrical charge and of the blocking ratio (3)) and ii) a change of the diffuse double-layer thickness.

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## **Ion Diffusion in the Electric Double Layer**

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Analytic expressions for the mean first passage times of ions diffusing in the electric double layer between two planar charged surfaces have been derived. The theory is based on the Smoluchowski-Poisson-Boltzmann model in which the diffusing ion is assumed to move in the potential field given by the non-linear Poisson-Boltzmann equation. Numerical results for the mean first passage times of co-ions and counter-ions calculated under the non-linear Poisson-Boltzmann model are given for a range of surface separations, surface potentials and ionic concentrations. Two simple analytic methods for calculating the mean first passage times are also presented.

THE DIFFERENCE IN THE MECHANISM OF DOPING AND UNDOPING OF A CONDUCTING  
POLYMER STUDIED BY ELLIPSOMETRY

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We used an optical model derived from that proposed by Gottesfeld et al.<sup>(1,2)</sup> to discriminate between the mechanism of the oxidation and the reduction of poly(3-methylthiophene) and to determine the rate of the participation of polarons and bipolarons to the process.

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# Dynamics of Lateral Diffusion Processes in Langmuir Monolayers at the Air/Water Interface

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Lateral diffusion of surfactants at the air/water interface is probed electrochemically with a novel one-dimensional micro-band electrode positioned at that interface. The fabrication of micro-band electrodes involves vapor-deposition of 50 nm thick, 5 - 1000  $\mu\text{m}$  wide strips of gold on microscope glass slides (ca. 1 x 2  $\text{cm}^2$ ). The entire surface of the glass slide with the gold film is then coated with a monolayer of octadecyltrichlorosilane (OTS) and octadecyl thiol. These steps render the surface hydrophobic exhibiting contact angles with water of  $110^\circ - 112^\circ$ . The actual preparation of micro-electrodes involves breaking the gold coated substrate along a line perpendicular to the gold strip thus producing two electrodes with freshly exposed 50 nm wide, ca. 0.1 cm long micro-band of gold. When a micro-band electrode is positioned at the air/water interface, a three phase "interface" is formed along the line between clean and the OTS-coated gold surface. Hence, molecules spread at the water surface are in contact with the micro-band electrode along this three phase line.

Electrochemical measurements of the dynamics of 2-D diffusion at the water surface were carried out with several electrochemically active amphiphilic derivatives of ferrocene and 4,4'-bipyridyl. The values of the diffusion coefficient depend strongly on the surface concentration of the amphiphile and range, for the case of an octadecylferrocene derivative, from  $2 \times 10^{-5} \text{ cm}^2/\text{s}$  at 400  $\text{\AA}^2/\text{molecule}$  to  $1 \times 10^{-7} \text{ cm}^2/\text{s}$  at 48  $\text{\AA}^2/\text{molecule}$ . The exponential in character decay of  $D$  vs  $\Gamma$  plots can be understood in terms of the free volume model of diffusion in fluids. A second channel of later charge transport in these types of assemblies involves electron hopping between the redox sites in surface monolayer. We will discuss these phenomena as a function of surface concentration, counter-ion effects and relative orientation of the redox sites.

# COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE ELLIPSOMETRIC PARAMETERS DESCRIBING THE ELECTROCHEMICAL INTERFACE

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The theoretical attempts to calculate the electronic properties of a metal-electrolyte interface can be specially well supported by ellipsometric measurements, provide they are carried out under severe experimental conditions very well defined (monocrystalline surfaces, specific adsorption avoided in situ accurate, optical measurements). Some results in this field were previously reported<sup>(1,2)</sup> on Ag(hkl) and Au(hkl) in NaF solutions.

Here our purpose is :

1/ To compare the optical behaviour of Au(hkl) on NaF and KPF<sub>6</sub> electrolyte, as to demonstrate that the ionic adsorption does not influence the optical measurements.

2/ To compare the experimental  $\Delta$  variations with those calculated through a microscopic model<sup>(2,3)</sup> as a function of  $\chi_o$  (surface dipole)  $d$  (closest approach distance between the inner layer and the jellium edge) and  $\sigma$  (surface charge density). The values of  $d$  were calculated by Amokrane et al on Ag (111)<sup>(4)</sup>.

3/ To show that, as we claimed elsewhere<sup>(1,2)</sup>, the "metal side" parameters can experimentally be separated from the "solution side" parameters, through suitable optical measurements.

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**ELECTRIC DOUBLE LAYER INTERACTIONS  
IN MEMBRANES AND COLLOID PARTICLES  
OF ARBITRARY SHAPES**

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**Abstract**

The properties of electric double layers near curved surfaces of arbitrary shapes and genus are obtained exactly within the Debye-Huckel regime by means of multiple scattering expansions. This allows the evaluation of the universal spontaneous ,scalar and Gaussian curvature contributions to the self-free energies of membranes .The interactions between two charged colloidal particles, also of arbitrary shapes, are calculated exactly from the multiple scattering expansions.

Session (4)

## Current Flow Through Open Biological Channels

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Most biological cells use electricity to help perform their natural functions: electrical signals transmit information in the nervous system and co-ordinate contraction in muscle; electrical current moves substances in the kidney, stomach, intestine, and endocrine glands; almost all cells control their size by controlling the movement of ions.

Biological cells are defined by their outer membrane, an impermeable structure that confines and protects the molecules of life. Current flows through membranes in protein molecules called channels. Channels contain a pore that is open or closed; the opening process (called "gating") is controlled by many variables of biological interest, e.g. voltage, drugs, sensory input, but too little is known of gating to allow much general analysis.

Once a channel is open, ions move through its pore much as they do in free solution, although some ions move more quickly (e.g.,  $10\times$ ) than others: channels are said to be selective for the ions which move quickest. Almost all channels are cation or anion selective; most are selective for one of the cations  $K^+$ ,  $Na^+$ , or  $Ca^{++}$ . The amount of current that flows (its "permeability") is a significant property of open channels, influencing many biological functions. Selectivity is the most important property of the open channel. The type of ion that permeates an open channel often determines its biological functions.

Many laboratories, including our own, routinely measure current flow through *single* channel molecules, but relatively little theoretical analysis of ion permeation has been done. Earlier theoretical work from our group (e.g., Quart. Rev. Biophysics 21:331, 1988) tries to apply the stochastic theory of chemical reactions (following Kramers, Wolynes, and Hynes, among others) to ion movement in open channels. That theory is a "mean field" theory describing the entire interaction of an ion and channel protein as the frictional movement of a particle in a *fixed* potential field.

The work described here evaluates the role of dielectric interactions between the ion and the channel wall. The channel protein is described by its dielectric constant, *not* by a fixed effective potential. The pore of the channel is described as a hole in a dielectric, filled with electrolyte solution. Current flow through the pore (i.e., the open channel) is described by the Nernst-Planck equations, allowing space charge, namely a violation of electroneutrality. The space charge creates a potential in the pore according to Poisson's equation and a potential in the wall of the channel according to Laplace's equation, linked by jump boundary conditions. The induced potential in the wall of the channel is *not* fixed—it depends on all the parameters of the problem—so the mean field theory previously used may, or may not, turn out to be an appropriate approximation.

Singular perturbation theory is used to solve these coupled (non-linear) partial differential equations, exploiting the long narrow shape of the channel. The analysis yields an integral equation for the potential distribution along the channel, easily computed in most cases. The distribution of potential determines the concentration along the channel and integrals over these distributions determine the current flow for a given potential and concentration gradient across the channel.

Results of these computations will be shown. The "mean field" approximation and the role of the dielectric constant will be evaluated. Experimental results will be discussed, and applications and extensions of the theory.

# A MODEL OF A DOUBLE LAYER: AN ELASTICALLY BONDED DIPOLE CAPACITOR

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The presented ideal model for a metal-electrolyte interface considers the ion-electron translational relaxation and the water dipoles reorientation simultaneously on an equal ground thus revealing principal features of their mutual interference. The model resembles those described in Ref.1. The Hamiltonian of the model is given by the expression:

$$H = (1/2)k(l-l_0)^2 + 2\pi\sigma\varphi - 4\pi\sigma P_x + 2\pi P_x \varphi/l - 4.81p \varphi/l^3 + \sum_{i,j} w_{ij}$$

(the notations are obvious). It can be shown<sup>2</sup> that the last term in this equation is comparatively small at  $a > l$  and negligible at  $a \gg l$  (here  $a$  is a lattice constant and  $l$  is the gap width). Omitting two last terms in the Hamiltonian, one gets the Watts-Tobin approximation.<sup>3</sup> Hence, the Watts-Tobin approximation<sup>3</sup> is exact in the limit  $a \gg l \gg 1$ , if the gap is allowed to relax, and in the limit  $a \gg l$ , if the gap is fixed.

Minimization of the free energy of the system (with pair interactions  $w_{ij}$  being neglected), leads to the following results.

1. Relaxation of the gap changes the behaviour of the dipole capacitor essentially. As a consequence, the degenerate critical point of the energy of the "global system", negative values and other capacity anomalies, instability under the potential control and other "flags of catastrophe"<sup>1</sup> are inherent in a dipole capacitor with a relaxing gap.
2. There are three different modes (a dipole capacitor mode, a gap relaxing mode and an anomalous mode) in the behaviour of the system at low enough temperatures, while at high temperatures the system resembles an elastically bonded capacitor with Ampere interaction.<sup>4</sup>
3. The predictions of the model (at  $a = l$ ) agrees with experimental data better, than in the previous models, but discrepancies are still very large.

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## CORRELATIONS IN DIPOL FLUIDS AND ION-DIPOLE MIXTURES

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As a model for a solvent and an electrolyte, we study fluids of hard sphere dipoles and mixtures of hard sphere ions and hard sphere dipoles. We calculate the correlation functions from the Ornstein-Zernike equation with RHNC-closure.

We investigate the quality of our correlation functions by analysing the dielectric function of the dipol fluid as well as the gas-liquid phase transition of this system.

To localize the coexistence curve in a  $p,T$ -phasediagram we need accurate methods for calculating the chemical potential as well as the pressure. We compare two ways to determine the chemical potential: On one hand via energy-temperature integration, on the other via density functional concepts.

For the electrolyte mixture, we study the ion dipole correlation in order to understand the polarisation and the polarisability in the solvation shell around an ion. Also the effect of ion concentration on the dielectric function is calculated. We hope to present also some results for the electrolyte interface.



## SECOND HARMONIC ELECTROREFLECTANCE SPECTROSCOPY

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Optical second harmonic generation (SHG) at the electrochemically controlled surface of Ag(111) has been measured using a tunable laser covering a range from 3.5 eV to 4.0 eV, in the second harmonic photon energy. We have emphasized the crystal orientation dependence of the applied voltage induced change in the SHG signal. This allows us to extract the second order electroreflectance coefficients through fits to a phenomenological model. We have interpreted the results by comparison to the expected modulation of dynamical screening and surface state energies.

This work was sponsored by the U. S. Department of Energy under grant DE-FG02-86ER45253.

SURFACE PLASMON ASSISTED RAMAN SCATTERING  
FROM ELECTROCHEMICALLY CONTROLLED ADSORBATES  
ON FLAT, SINGLE CRYSTAL SILVER

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We have used the Kretschmann configuration to couple to both the incident and scattered radiation in the Raman process involving molecules in contact with Ag which faces an electrochemical solution. The Ag was a single crystal (111) film grown on mica and, as such, represents the most ideal smooth surface which can be produced. Our device exploits collection of the entire emission cone and a super-cooled photodiode array detector. These features have led to signal-to-noise ratios in excess of 400 from an adsorbed monolayer of para-nitrosodimethylaniline (pNDMA) using an incident power as low as 6 mW (514.5 nm). We have used the adsorption site sensitivity of pNDMA to characterize various types of mild Ag surface treatments common to surface enhanced Raman scattering technique. We find that all of the roughening methods lead to heterogeneities not observed on the single crystal surface.

This work was sponsored by the U. S. Department of Energy under grant DE-FG02-86ER45253.

ANOMALIES IN UNDERPOTENTIAL DEPOSITION  
REVEALED WITH THE QUARTZ CRYSTAL NANOBALANCE

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Our crystal oscillator electrochemical mass detector has a sensitivity of one nanogram/cm<sup>2</sup>. It has been applied to measurements of the correlation between charge transfer and mass accumulation in underpotential deposition of Tl on Ag and of Cd on Ag. In the case of Cd we observe an electrosorption valency of two for the first 1.5 monolayers, which are adsorbed in several separate steps. By contrast, Tl demonstrates a coverage dependent electrosorption valency which ranges from two to unity during the growth of the first monolayer, remaining at the expected value of one through deposition of the second monolayer. This is the first report of a superequivalent charge transfer in a process of this type.

This work was sponsored by the U. S. Department of Energy under grant DE-FG02-86ER45253.

SURFACE EXTENDED X-RAY ABSORPTION FINE STRUCTURE  
OF COPPER ON A PLATINUM ELECTRODE

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We have developed a thin-layer electrochemical EXAFS chamber designed for a sample with a surface area of  $55 \text{ cm}^2$ . It has been used in a grazing incidence, fluorescence detection mode to study the environment of one monolayer of Cu, in the underpotential condition, on Pt. Our signal intensity is sufficiently large that we are able to detect details in the spectra not previously recognized in experiments of this type. In addition to these more subtle effects, we have determined that the near neighbor to the Cu is oxygen, most probably associated with water in a well-defined surface configuration. This is observed even with the x rays polarized parallel to the surface. These data are consistent with water adsorbed in hollow sites between Cu adatoms.

This work was sponsored by the U. S. Office of Naval Research under grants N00014-87-K-0551, N00014-90-J-1332, and N00014-90-J-1326. The measurements were accomplished at the National Synchrotron Light Source on beam line X9A, built and operated by the National Biostructures Principal Research Team.

# ELECTROLYTE STRUCTURE INSIDE A CHARGED CYLINDRICAL PORE

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## A B S T R A C T

The hypernetted chain/mean spherical (HNC/MS) equation is solved for a 1:1 and 2:2 restricted primitive model (RPM) electrolyte inside a charged, cylindrical pore. The density profiles are obtained and compared to those obtained from the Poisson - Boltzmann (PB) equation for the same model and to those obtained from the three point extension hypernetted chain/spherical (TPE HNC/MS) equation for a RPM electrolyte in a charged slit.

\* On leave from the Departamento de Física, UAM-I.

## Random Walks and the Double Layer Impedance

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### Abstract

The double layer impedance between a perfectly polarizable metallic electrode and an electrolyte exhibits anomalous behavior as a function of frequency  $\omega$ . This behavior is related to the surface roughness of the electrode. We introduce a random walk algorithm for calculating this behavior as a power series in  $(1-i\omega)^{-1}$ . We apply this algorithm to the calculation of the impedance corresponding to two different shapes of two dimensional electrodes: slots and diffusion-limited aggregates. In the first case, the calculated impedance shows the expected  $\omega^{-1/2}$  constant phase angle behavior. The impedance of the aggregates shows more complex behavior.

Session (1)

# **STRUCTURAL AND ELECTRIC PROPERTIES OF AN ION-DIPOLE FLUID IN CONTACT WITH CHARGED OR UNCHARGED HARD WALL. APPLICATION OF THE OPTIMIZED CLUSTER EXPANSIONS**

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An ion-dipole model of electrolyte solution near a charged or uncharged hard wall is considered. The surface is formed within Henderson-Abraham-Barker procedure. In order to investigate the structural and electric properties of the system, the optimized cluster expansions are applied. Actually, they are given as a double perturbation series respectively to the linearized theory (MSA/MSA) for the bulk model and the model in a contact with charged hard wall. The reference fluid separation and application of screening by non-point particles are essential within the construction. On the contrary to the simplest exponential approximation, the many-body correlation terms are allowed for. It is shown that this is important for the systems with more intensive interactions. Besides the traditional classification by the field vertices number, an integral equation which provides generation of many-body correlation terms for the distribution functions is proposed. An iterative scheme to solve the integral equation looks similar to the truncated reference HNC theory.

The density profiles of ions and dipole molecules, the charge and polarization profiles, the angular distribution of dipoles in the surface layers are calculated. The dependencies on the ion concentration, dipole moment value and the electric field are studied. The comparison with other theories and computer simulation data for aqueous systems near the metal wall is given. Finally, the pair distribution function of electrolyte particles near charged wall in the more sophisticated form than the superposition approximation is investigated.

# PREDICTED, TENDENCY IN SWELLING PRESSURE MEASUREMENTS FOR LITHIUM, SODIUM, POTASSIUM, RUBIDIUM AND CESIUM MONTMORILLONITE.

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## ABSTRACT

Swelling Pressure ( $\Pi$ ) in different clay systems immersed in electrolytic solution has been calculated. Specific adsorption considerations were not included in order to evaluate only the effects of the size of the electrolyte on the swelling pressure in clay-water dispersions. An increment in the swelling pressure values compared to the Gouy-Chapman results has been observed. We have used a simple model that evaluates separately the effects of the size of the electrolyte. A strong dependence of swelling pressure on the size of the counterion was noted. We have made use of three different sets of size parameters found in the literature to show that the predicted tendency in the variation of the swelling pressure for the set of lithium, sodium, potassium, rubidium and cesium montmorillonite depends extremely on the size parameter set that has been chosen from the literature.

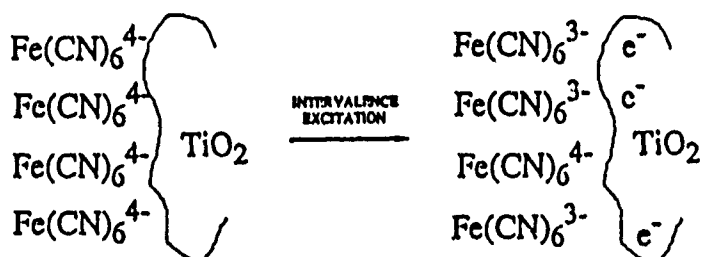


Surface Intervalence Enhanced Raman Scattering.  
Complete Mode-by-Mode Assessments of Franck-Condon  
Barriers to Interfacial Charge Transfer.

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One of the key requirements in any quantitative description of electron transfer kinetics, in any environment, is an accurate estimate of internal or vibrational reorganization energies. We have recently shown experimentally that a complete mode-by-mode assessment of vibrational reorganization for intramolecular ET can be obtained for several systems via intervalence-enhanced Raman scattering.<sup>1</sup> The relevant theory is the time-domain analysis devised by Heller and co-worker.<sup>2</sup> This talk will describe the intramolecular ET experiments along with very recent results for surface intervalence charge transfer from adsorbed transition-metal species to colloidal titanium dioxide particles.



In our experiments, the surface intervalence charge-transfer maximum for absorption by  $\text{Fe(CN)}_6^{4-}/\text{TiO}_2(\text{colloid})$  at pH = 3 is ~410 nm, in agreement with the very recent work of Vrachnon, et al.<sup>3</sup> Resonant or preresonant intervalence excitation yields a surprising result: surface as well as adsorbed reactant modes are enhanced. This indicates that both the surface and the molecular reactant are subject to vibrational reorganization during the interfacial charge transfer process. Quantitative results (i.e. bond length changes, force constants, intrinsic barrier heights, etc.) from this study and others will be presented.

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**LASER-INDUCED ELECTRODEPOSITION OF  
TRANSITION METALS ON SILICON**

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Laser-induced structured deposition of narrow transition metal traces was studied on p-type single and poly-crystalline silicon in an aqueous Schottky-junction configuration. Metal patterns generated in a computer-controlled scanning laser spot apparatus matched closely the beam trace of the scanning focused cw Krypton ion laser. The influence of the potential, the laser parameters, and the status of the interfacial oxidic layers on the electron transfer, the nucleation and growth rate, and the MIS-junction characteristics were studied. The illuminated and metallized areas exhibited various charging effects of interfacial electronic states. This, and their implication for structured laser induced deposition is discussed.

# PHOTOELECTROPHORESIS OF COLLOIDAL SEMICONDUCTORS

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Aqueous dispersions of colloidal semiconductor particles have been used as photocatalysts in a number of reactions, such as the oxidation of  $\text{CN}^-$  ions with  $\text{O}_2$  at  $\text{TiO}_2$  particle surfaces and the decomposition of ethene and ethyne acids at platinized  $\text{TiO}_2$  to generate molecular hydrogen. Such reactions are thought to occur initially by the absorption of ultra-band gap light in the semiconductor to form electron-hole pairs ( $e^-$ ,  $h^+$ ) which may then react with the solvent, solution species or lattice sites. Any difference in the kinetics of the two redox reactions involving photogenerated electrons and holes, due for example to the catalytic properties of the particles, will lead to a photogenerated change in particle charge. The poster/paper will describe the development of a technique to detect this as a change in particle velocity ( $v_E$ ) in an applied electric field ( $E$ ) - **photoelectrophoresis**.

A Malvern Zetasizer IIc laser Doppler electrophoresis apparatus was modified to accept light from an 900 W xenon lamp via a monochromator and fibre optic light guide into the electrophoresis cell, to enable (photo-) electrophoretic mobilities ( $u_E = v_E / E$ ), which can be related to particle charge, to be determined as a function of wavelength of exciting radiation and illumination time.

Photo-induced changes in electrophoretic mobilities of aqueous dispersions of colloidal  $\text{TiO}_2$  will be reported as functions of time, pH, wavelength and intensity of light, applied electric field and concentrations of hole ( $\text{Cl}^-$  and  $\text{Br}^-$ ) and electron ( $\text{MV}^{2+}$  and  $\text{O}_2$ ) scavengers. In addition, the behaviour of colloidal  $\text{TiO}_2$  in the presence of adsorbed  $\text{Fe}(\text{CN})_6^{4-}$  photosensitizing species,  $\text{SnO}_2$  and  $\text{Ti}_4\text{O}_7$  ("Ebonex") will be described. As the light-on and light-off changes in particle mobility occurs over say 10 - 1000 s, the photogenerated charge change is primarily ionic rather than electronic in nature. Hence, potential-pH diagrams were calculated and the positions of the band edges as functions of pH included, to aid assignment of the likely reactions of photogenerated holes and electrons in such systems.

A pseudo-first order kinetic model will be described to explain the accumulation of positive charge at pHs below the isoelectric point (pH 5.8) of illuminated colloidal  $\text{TiO}_2$ , both in the absence and presence of hole scavengers such as chloride ions; this enabled the rate constants for the various reactions to be determined. A second order kinetic model for  $\text{TiO}_2$  will also be reported; its use in analysing experimental photoelectrophoresis data provided further insight into the valence band hole driven water oxidation.

# Effects of Electrical Double Layer on Photoinduced Electron Transfer Quenching of $\text{Ru(II)(bpy)}_3^{2+}$ Derivative in LB films.

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We have studied LB film molecular assemblies with spatial regularity and examined their properties for photoelectric conversion.<sup>1)</sup> In connection with this photoelectric conversion device, we have studied the photoinduced electron transfer kinetics in the LB films containing the sensitizer(S) and the electron donors(D) with different standard redox potentials,  $E^\circ$ 's.<sup>2)</sup> However, contrary to our expectations, photoinduced electron transfer quenching was observed even in S/D LB systems in which the electron transfer seemed to be an up-hill reaction based on the energy levels determined by the halfwave potentials,  $E_{1/2}$ , in acetonitrile.

This unexpected result can be interpreted as follows. The counterions were incorporated into the LB films. Owing to the electric double layer formed in the LB films, the standard free energy of the electron transfer quenching,  $\Delta G^\circ$ , based on  $E_{1/2}$  should be modified by taking account of the electric potential difference,  $\Delta\phi$ , generated between the sensitizer and the donor.

In the present work, three kinds of amphiphilic ferrocene derivatives as donors with the same  $E^\circ$ , the same alkyl chain spacer, and the different charges (+1, 0, -1) at the hydrophilic head groups were newly synthesized. As the sensitizer, a  $\text{Ru(bpy)}_3^{2+}$  derivative with two nonadecyl chains was used as previously.<sup>3)</sup> Three kinds of LB films in an S/D form were deposited on quartz with the different donors. By using nanosecond laser photolysis, the luminescence decays were measured for these S/D systems. We will discuss the electron transfer kinetics for these systems in terms of the corrected energy gap,  $\Delta G^\circ$ , including  $\Delta\phi$ .

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## Jellium Theory of the Second Harmonic Generation from the Electrochemical Interface

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In this communication we present first results on the theoretical study of the second harmonic generation (SHG) from the electrochemical interface.

We assume that the main contribution to the optical nonlinear polarizability of the interface is given by the subsystem of the quasi-free electrons of the metal. We thus can extend the theory of SHG from the metal surfaces<sup>1</sup> to the metal electrolyte case because the medium which is bounding the metal influences the result only via the modification of the surface electronic profile and its response to charging.

For the calculation of the surface electronic properties we apply the trial function version of the density functional formalism. The obtained simple expression for the SHG-signal through the first and the second derivative over the electrode charge  $\sigma$  of the center of mass of the excess charge distribution,  $z_\sigma$ , can then be used with  $z_\sigma$  to be determined subject to the model of the metal/medium interaction. The latter can be done with the use of the experience accumulated in this field with treating such models as including the interfacial relaxation and ionic adsorption (for review see <sup>2</sup>).

In contrast to metal/vacuum, at the electrochemical interface there is a new variable: the electrode charge  $\sigma$ . Our main goal was thus to study the  $\sigma$  - dependence of SHG - signals and the effect of the medium on its shape. We show that the latter changes the signal drastically as compared to the metal/vacuum interface. The typical curves can be well distinguished depending on the picture of the metal/medium interaction. Thus, the SHG-signal can be a very sensitive tool for the study of its main features. For instance, it is very sensitive to the ionic adsorption (essentially more sensitive than plasmon resonance<sup>3</sup>). It will be very challenging to verify the predictions of this theory in experiments.

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# On the Quantum Properties of Adsorbed Particles Within the Model of a Hydrogen Atom Near a Hard Wall

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A problem of a hydrogen atom near a hard wall is considered in order to study a modification of the quantum structure of particles in a contact with a surface. The model can be used to describe impurities or excitons near a crystal boundary as well as atoms and molecules adsorbed on a semiconductor surface.<sup>(1-3)</sup> It is applicable as much as a surface is considered to be impenetrable. An exact solution of the Schrödinger equation for the hydrogen atom near the hard wall is given in the adiabatic approximation. The energy spectrum and the set of semi-infinite hydrogen wave functions are obtained<sup>(4)</sup> The dipole matrix elements between those eigenfunctions are calculated. The dipole moment and the oscillator strengths dependent on the distance from the wall are obtained. A set of asymptotics for energy, the wave functions, and the matrix elements at large separations from the surface are investigated. A hydrogen molecule is considered in the framework of Heitler-London method. An approximate form for the atom-wall and atom-atom interaction potentials near the wall are proposed. The set of semi-infinite hydrogen atomic orbitals is proposed to investigate more complicated atoms and molecules. Adsorption on a surface which possesses a certain structure is discussed.

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MEASUREMENT OF WATER ENTROPY AS A FUNCTION OF DISTANCE FROM DNA  
MOLECULES

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Restructuring of water by polar surfaces has been the subject of extensive discussion in the recent years. This effect, presumed in colloid science many years ago, is probably a central feature of hydration forces as well as of many other properties of electrified interfaces. No direct experimental data on it, however, have been available up to now. We have recently applied Maxwell relationships and a Clausius-Clapèyron equation to the temperature sensitive forces in DNA assemblies measured by the osmotic stress method. We have mapped the temperature dependent force-distance curves and transformed them into water entropy and system enthalpy vs. separation relations of DNA molecules. Indeed, the entropies and enthalpies derived from force measurements are far more rigorous, in principle, and often more accurate, than those inferred from calorimetry based on many ad hoc assumptions. We have found that water entropy increases exponentially with the distance from DNA surface. This is the first direct evidence of the exponentially decaying structuring of water by a polar surface.

## NEW APPROACH IN THEORY OF HYDRATION FORCES

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In recent years detailed experiments have revealed new qualitative features of hydration forces, which could not be described by the traditional theories. It has been shown, in particular, that the decay length of the force, previously thought to be determined by intrinsic water properties, is actually strongly dependent on the structure of the interacting surfaces. Evidence of the hydration attraction has also been found in some systems. An important property of the systems studied is that almost all of them have at least two types of polar groups, presumably orienting water in opposite directions, attached to each surface. In the present work we show that in these systems qualitative features of the hydration force are more sensitive to intra- and intersurface spatial correlations in the distribution of the polar groups rather than to properties of water or physical nature of a force field created by surfaces (electrostatic field or "field" of order parameter in water). Between disordered surfaces, hydration forces are purely repulsive. With the increase of the lateral intrasurface ordering, the decay length of the force decreases. When ordering reaches a critical value, the intersurface correlations become strong enough to provide hydration attraction at large distances. Further increase in the lateral ordering leads to strengthening of the attractive part of the interaction and full crossover from repulsion to attraction. These theoretical predictions explain the observed dependence of the force parameters on the surface structure as well as some very peculiar phenomena observed in lipid systems such as strengthening of the force with decrease in the surface density of polar groups, responsible for the interaction. This strengthening occurs upon the melting of lipid hydrophobic chains or the mixing of lipid molecules with molecules of diacylglycerol.



## **Lateral charge transport in Langmuir-Blodgett films of electroactive amphiphiles.**

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An array of interdigitated microelectrodes is deposited on glass substrates using photo-lithographic techniques. The pattern of the microelectrodes consists of fifty pairs of generator/collector electrodes, each of which is nominally 80  $\mu\text{m}$  long, 4  $\mu\text{m}$  wide, and is spaced by 4  $\mu\text{m}$ .

Amphiphiles with electroactive headgroups have been transferred onto these types of electrodes using the Langmuir-Blodgett technique. The electrochemical characteristics of these assemblies are discussed. In particular, the investigations will focus on the lateral charge transport process and how it is affected by:

- substrate/amphiphile interactions
- surface coverage
- temperature
- the oxidation state of the amphiphilic molecules

A monolayer of octadecylferrocene transferred to an electrode surface treated with octadecyltrichlorosilane (OTS) constitutes an amphiphilic bilayer that resembles a cell membrane. Preliminary results for this assembly in 1 M  $\text{HClO}_4$  yield an apparent diffusion coefficient of  $3\text{--}5 \cdot 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$  for a surface coverage of the electroactive amphiphile of  $1\text{--}2 \cdot 10^{-10} \text{ mole cm}^{-2}$ . The diffusion coefficient is estimated from the steady state current as obtained when the collector electrode is held at a constant potential where the ferrocene is completely reduced and the generator potential is swept with a low scan rate to a potential beyond the oxidation wave.

EFFECTS OF ADSORBED  
AND UNADSORBED IONS ON THE  
Si-O VIBRATIONS IN MONTMORILLONITE

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The basal oxygens of interlinked silica tetrahedra compose the surfaces of montmorillonite, a common clay mineral. Since adsorbed cations are in close proximity to these surfaces, the postulate was made that they would alter the vibrations of the Si-O dipoles in the silica tetrahedra to a degree depending on their energy of adsorption. To test this postulate, suspensions were prepared by mixing Li-, Na- and K-saturated montmorillonite in different proportions with solutions having different concentrations of the respective chloride salts. Also, suspensions were prepared by mixing Na-saturated montmorillonite in different proportions with solutions having different concentrations of NaCl, NaBr and NaI. Then each suspension was put in a cell having Irtran windows and a variable path-length,  $l$ ; the absorbance,  $A$ , was measured at the frequency of Si-O stretching ( $\sim 1040\text{ cm}^{-1}$ ); and the specific absorptivity,  $\epsilon$ , was calculated by means of the equation  $A = \epsilon cl$ , where  $c$  is the concentration of the montmorillonite in  $\text{g/cm}^3$ . It was found that the magnitude of  $\epsilon$  decreased with increasing electrolyte concentration and with increasing crystallographic radius of the adsorbed cation. However, the magnitude of  $\epsilon$  was not affected by the nature of the anion of the electrolyte. These findings were used to elucidate the structure of the electric double layer and the factors that affect it.

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### Redox Reaction Mechanisms at the AgCl/Chlorine Gas Interface

The exchange reaction of chlorine at the gas/solid interface between AgCl and a chlorine atmosphere has been investigated by employing the following galvanic cell:

Ag/Ag<sup>+</sup> ion conductor/AgCl, Cl<sub>2</sub>, Pt.

The change of the voltage upon a change of the applied parameters such as the chlorine partial pressures, temperature, gas composition and dopant concentrations of AgCl has been analyzed in order to provide insight into the redox process of chlorine exchange between the gaseous phase and AgCl.

Emphasis will be given to the kinetics of the variation of the response behaviour upon changes of the chlorine partial pressure. The application in chemical gas sensors will be discussed.

## **THE ELECTRICAL DOUBLE LAYER. NONLOCAL FREE ENERGY DENSITY FUNCTIONAL APPROXIMATIONS**

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### **ABSTRACT**

This work is an overview of some recent work on the development of some nonlocal free energy density functional approximations for the primitive model of the electrified interface. Using a perturbative scheme, the hard-sphere term of the free energy functional is based on a nonlocal generic model functional proposed by Percus. The electrostatic part of the ion-ion direct correlation function for the inhomogeneous electrolyte in the interfacial region is approximated by the mean spherical approximation for the bulk electrolyte. The results for the density profiles and diffuse layer potentials are compared with those of the Gouy-Chapman theory and Monte Carlo simulations. For highly charged surfaces, the profiles clearly show the layering effect present in the Monte Carlo data of 1:1 salts. The theory also predicts the charge inversion phenomenon which appears in the Monte Carlo results for some 2:2 and 2:1 salts.

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**ELECTRONIC STRUCTURAL CONTROL OF ELECTRON TRANSFER KINETICS**

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Current techniques of quantum chemistry make possible a detailed evaluation of the role of electronic structure in controlling electron transfer kinetics. Using the results of detailed quantum mechanical calculations in conjunction with suitable dynamical models, we analyze the kinetics of bimolecular electron transfer reactions for various transition metal redox systems. The reaction mechanisms are cast in the form of super-exchange coupling of donor and acceptor species. The analysis includes consideration of the dependence of coupling strength on the relative orientation and spin-state of reactants, as well as the role of solvent.

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# AN INTEGRAL EQUATION STUDY OF THE ELECTROKINETIC FLOW IN A NARROW SLIT PORE

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The application of pressure and/or potential gradients across charged capillaries, in equilibrium with a reservoir containing an electrolyte solution, gives origin to interesting electrokinetic phenomena. Namely, electroosmosis, streaming potential, capillary conductance and electroviscous retardation. The importance of the accurate description of this effects lies on its immediate applicability in the modeling of a wide variety of fundamental porous media in Chemistry, Engineering and Medicine that ranges from underground oil reservoir rocks, sand beds, molecular sieves, organic tissues, blood micro capillaries, to zeolite catalysts.

The classical work of Smoluchowski gives the basic description of the flow of an electrolyte solution through an infinitely wide pore. The existing electrostatic corrections for narrow capillaries are based on the solution of the Poisson-Boltzmann equation (MPB) that models the ions as point charges. In this work, the distribution of ions of finite diameter ( $a$ ), inside a charged planar slit micro pore, at fixed arbitrary zeta potential ( $\zeta$ ) and bulk salt concentrations ( $c$ ), is described using the three point extension of the HNC/MSA integral equation. This approach is known to give a good description of the structure of the single planar Electrical Double Layer.

The electrokinetic properties are evaluated through the corresponding Onsager coefficients, for a physically significant range of zeta potentials, pore sizes and salt concentrations of a 1-1 restricted primitive model electrolyte. The agreement between the classical result for point ions (MPB) and the HNC/MSA theory is good only for large pores ( $\tau \gg 9a$ ), low concentrations ( $c < 0.1M$ ) and low zeta potentials ( $\zeta < 25$  mV). However, as a consequence of the ionic exclusion, interesting effects on the electrokinetic properties were found, when the pore size becomes of molecular dimensions. These effects become very important for high concentrations and/or high zeta potentials.

A mean-field analysis of an ion-dipole mixture against a charged hard wall with specific dipole adsorption

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The electric double layer is modelled by a hard sphere ion-dipole mixture against a uniformly charged plane hard wall with specific adsorption of the dipoles at their distance of closest approach to the wall given by Baxter's sticky potential. The model is analysed in the mean field approximation for two ionic species and one dipole species, each species having a different diameter. A classification of some differential capacity curves  $C_D$  can be given on the relative sizes of the molecular radii and the strength of the adsorption coefficient.

Agreement with the experimental  $C_D$  results for Hg/LiAsF<sub>6</sub> with solvent tetrahydrofuran (THF) is obtained over the whole range of the experimental concentration and surface charge. The corresponding inner layer capacity  $C_i$  is also investigated for Hg/LiAsF<sub>6</sub> in THF. At low electrolyte concentration in the neighbourhood of the position of zero charge the  $C_i$  become very large, with the maximum in the peak increasing as the concentration is lowered or the temperature decreased. This anomalous behaviour in  $C_i$  is analogous to that occurring in many experimental situations.

# An Ising Type Model for the Electric Susceptibility of Transmembrane Ion Channels (TMIC)

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Structural influences on the electric susceptibility of TMIC are discussed using a model which simulates the water molecules in the channel by a chain of  $N$  point dipoles arrayed along the  $z$  axis normal to the planar surfaces of the membrane. The membrane is modeled by a uniform slab occupying the region  $0 \leq z \leq N\lambda$  ( $\lambda \sim 3\text{\AA}$  is the diameter of a water molecule) with dielectric constant  $\epsilon_M (=2)$ . For the external medium (electrolyte) we assume  $\epsilon_{EL} = \infty$ . The penetration of an ion into the channel is described by replacing the point dipole at the site  $n=I$  ( $1 \leq n \leq N$ ) by the point charge  $q^I$ .

The electric potential can be calculated by the method of images; each dipole  $p^n$  (or charge  $q^I$ ) produces an infinite chain of images with the period  $2N\lambda$ . The system Hamiltonian includes the interaction of ion and dipoles with one another and with an external field  $E_z$  and the interaction of each particle with the complete set of images. Using this Hamiltonian statistically averaged quantities such as  $\langle p_z^n \rangle$ ,  $\langle p_z^n p_z^m \rangle$ , etc are calculated for  $N=8$ . We compute these averages by direct summation over allowed configurations and by a Monte Carlo approach. For  $p_z^n$  the analogs of  $s=1$ ,  $s=2$  and  $s=4$  Ising Model are treated (three, five and nine allowed orientations respectively).

The following points should be emphasized:

- The electric susceptibility  $\chi^n$  and induced dipole moment  $\langle p^n \rangle$  depend on the position of the dipole, varying about 10-20% along the chain;
- In the presence of an ion we find a measurable reduction of the field-induced dipole moments and susceptibility (a kind of saturation effect). For example, at low external field the average susceptibility for an ion near the water-channel interface ( $I=1$ ) is reduced  $\sim 4$ -fold, indicative of a significant decrease of the effective dielectric constant of the channel! This effect is ion position dependent.

These results may be of significance in the analysis both of interactions between different species and of transport phenomena in TMIC.



AMORPHOUS SEMICONDUCTOR-ELECTROLYTE JUNCTION. ENERGETICS AT THE  
a-WO<sub>3</sub>/ELECTROLYTE JUNCTION.

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The knowledge of the energetics at the semiconductor/electrolyte junction is a fundamental task in order to understand the kinetics of charge transfer at such an interface (1). Although the qualitative predictions based on the theory of electron transfer at single crystal semiconductors are confirmed, in the last years some new features were observed in the case of amorphous semiconductors (a-SC)/electrolyte interfaces (2). This fact has raised up the necessity of a new approach to the study of the a-SC/electrolyte interface.

Recently we suggested a novel approach to the study of the energetics at the a-SC/electrolyte interface (3) based on the theory of a-SC Schottky barriers. The results of our investigation have shown that the use of the theory valid for monocrystalline semiconductors for characterizing the amorphous oxide/electrolyte junction leads to some discrepancies in the location of the energetic levels at the interface.

In this work we present a critical reexamination of the energetics at the a-WO<sub>3</sub>/electrolyte junction based on an admittance study performed in a large frequency range ( $3 \text{ Hz} \leq f \leq 3 \text{ kHz}$ ) both in aqueous and in acetonitrile solutions. The characteristic energy levels, the Fermi level and the mobility edges of the oxide, are derived in agreement with the theory of a-SC Schottky barriers. Moreover, the distribution of localized electronic states (DOS) around the Fermi level will be presented.

The possible influence of the anodization process on the DOS will be discussed in order to explain the influence of film thickness on the kinetics of electron transfer to redox couples in solution (4).

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# **EFFECTS OF LATERAL INTERACTIONS IN MULTICOMPONENT ADSORPTION**

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## **Abstract**

Effects induced by effective lateral interactions have been studied in a three-state lattice-gas model for two-component adsorption. In different regions of the space of interaction constants this model may exhibit either poisoning behavior or enhanced adsorption. We have demonstrated that these different behaviors are intimately related to the topologies of the phase diagrams for different values of the interactions. Based on this understanding we have developed quantitative criteria that predict the interaction strengths for which these types of behavior occur. Adsorption isotherms were obtained from numerical transfer-matrix and Monte Carlo calculations for a number of specific examples. In particular we have used this model to study the poisoning by sulfur of hydrogen adsorbed on Pt(111) in an acid aqueous environment and, as examples of enhanced adsorption, the adsorption of naphthalene on Cu and n-decylamine on Cu and Ni electrodes. In all these cases the agreement with experimentally obtained adsorption isotherms is good.

# The Vibrational Spectrum of Thiocarbonyl on Platinum Electrodes: Experiment and Theory

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The vibrational properties of carbon monoxide adsorbed on electrode surfaces have been studied extensively. Thiocarbonyl, CS, is of interest as a comparison to carbon monoxide adsorption since the two molecules are isoelectronic. However, due to the differences in their molecular orbital energies, CS is both a better  $\sigma$  donor and  $\pi$  acceptor than CO. Thus, a comparison of the vibrational spectra of CO and CS adsorbed on a platinum electrode should reflect the relative effects of  $\sigma$ - $\pi$  interactions between the surface and adsorbate.

The electrochemical reduction of carbon disulfide in acetonitrile provides a source of thiocarbonyl near the electrode surface, thus providing the first infrared spectroscopic evidence for electrode-adsorbed thiocarbonyl. In analogy to adsorbed CO the adsorbate was assigned to the one fold on-top site. A potential-induced change in the C-S stretching vibration of  $10\text{cm}^{-1}/\text{V}$  was observed for adsorbed CS.

The experimental results were simulated using both a classical and the Atom Superposition Electron Delocalization (ASED) molecular orbital methods. The greater  $\sigma$  donor/ $\pi$  acceptor properties of the thiocarbonyl molecule with respect to carbon monoxide are apparent in both simulated results. The classical model predicts a potential-induced shift for the C-S vibration of  $16.9\text{cm}^{-1}/\text{V}$ , while the ASED method predicts  $16.8\text{cm}^{-1}/\text{V}$ . The discrepancy between these calculated values and the experimental rate of  $10\text{cm}^{-1}/\text{V}$  is attributed to the influences of the solvent at the interface, i.e., in that the dielectric properties of the solvent and its ability to penetrate into the adsorbate layer determining the strength of the electric field across the adsorbate layer. However, the agreement between the tuning rates predicted by the classical calculation, with the Stark type perturbation, and the ASED molecular orbital method indicates that the electrochemical Stark effect takes precedence over the chemical bonding explanation for the shift in frequency of the C-S stretching vibration with applied potential.

INTERACTION OF TWO SPHERICAL DOUBLE LAYERS: EXACT NUMERICAL  
SOLUTION TO THE POISSON-BOLTZMANN EQUATION.

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A B S T R A C T

In the point ion limit, the three point extension hypernetted chain/mean spherical (TPE HNC/MS) equation for the interaction of two spherical colloidal particles in an electrolyte, reduces to the corresponding integral equation version of the non-linear Poisson-Boltzmann (PB) equation. We numerically solve the PB equation for various colloidal particles radii, charge densities and distance separations. The linearized PB results for the colloidal particle interaction force are recovered for small ionic concentrations and/or small colloidal particles radii and/or large colloidal particles separations. To be noticed is the oscillatory behavior of the point ion density profiles at high ionic concentrations.

## **Abstract**

**Rigid dipole orientation at fluid interfaces, role of the dielectric constants, of the relaxations and of the cooperativity. A thermodynamic approach**

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A theoretical extension of the thermodynamics of interfacial dipole layers is presented in order to show the role of the dielectric constants on the orientation affinity. By comparing the affinities corresponding to two couples of different media for the same dipolar orientation, we evidence a linear dependence of the difference of the affinities with the difference of the reverse mean dielectric constants.

Experiments performed by L. Lavielle et al. (CNRS Mulhouse) on grafted polyethylene and polypropylene in different liquids show a good correlation between theoretical and experimental results.

Surface relaxation and cooperative orientation induced by an electrochemical field are also discussed in the frame of our theory.

## **Halogen, Alkali and Hydrogen Coadsorption with Water on Metal Surfaces**

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The experimental concept of simulating the metal-electrolyte interface by adsorption of solution components onto metal surfaces in UHV is briefly reviewed. Three coadsorption systems involving electrochemically relevant ionic species, interacting with water, are described to illustrate the detailed microscopic insight provided by this approach:

1. The electrostatic potential drop in the inner layer for specifically adsorbed chloride and bromide on Ag(110) is shown to be very similar in situ and in UHV.
2. A novel experimental concept for directly determining, at least formally, the dielectric constant of water in the double layer is exemplified by cesium-water coadsorption studies on Cu (110).
3. The recent contention that coadsorbed atomic hydrogen and water may react to form hydrated protons on metal surfaces cannot be reconciled with our TDS and EELS results for isotopic substitution of the adsorbates.

# THE APPARENT BARRIER HEIGHT FOR TUNNELLING IN THE STM THROUGH LIQUIDS: INITIAL CONSIDERATIONS

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The lowest non-bonding level in liquids, usually termed  $V_O$ , has been the subject of intense interest in radiation chemistry, because the transition from the quasi-free to the solvated state is an important step in the energy degradation of electrons generated by radiation. Conceptually, this  $V_O$ -level may be equated to the vacuum level and must therefore be considered as a crucial quantity when measuring the barrier height for tunnelling through liquids.

One of the most interesting applications of scanning tunnelling microscopy in a liquid environment is undoubtedly the study of the metal-electrolyte interface. However, in studies performed during the past few years the barrier height problem has been somewhat neglected. In this contribution we shall discuss the mechanisms of tunnelling through condensed media and we shall consider in particular the role that the  $V_O$ -level and the energy level of the solvated electron play in promoting the tunnelling in the STM-gap. A variety of experimental results will be presented and analyzed in the light of our novel conceptual approach to tunnelling in a liquid environment.

# Electrochemical Behavior of Gold Electrodes Modified with Ferrocenylalkanethiol by Self-assembling Method

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Studies of the chemical modification of solid surfaces have been carried out very extensively. Langmuir-Blogett (LB) method has been the most popular technique to form functionalized solid surfaces. Unfortunately, the stability of the LB layers is sometimes low because the modified molecules adsorb on the solid surface only physically. To overcome this difficulty, the preparation of functionalized surface by self-assembling method is currently investigated by many groups. In this process, organized layer of functional molecules is formed on the solid surface with chemical bonding between the molecules and the surface.

In this study, we attempted to modify gold surface with ferrocenylalkanethiol by self-assembling method and report the electrochemical behavior of the surface in various solutions.

We used gold films (thickness = 1200Å), which is vacuum deposited on glass at 300°C, as substrate. Ferrocenylalkanethiols were synthesized from ferrocene and corresponding bromoalkanoic acid. Modification of gold surface was carried out by soaking the gold substrate in a hexane solution containing ferrocenylalkanethiol for various period. After this process, the modified gold was washed with hexane and, then, with water.

The cyclic voltammogram (CV) of the modified gold electrode was obtained in 1M HClO<sub>4</sub> solution. The CV shows very symmetrical waves with oxidation peak at +330 mV (vs. SSCE) and reduction peak at + 320 mV. A linear relation was observed between sweep rate and peak current. These results suggest that the electrochemical response was by attached ferrocene groups. The number of adsorbed molecules is calculated from the peak area as  $5.6 \times 10^{14} \text{ cm}^{-2}$  in the case of ferrocenylhexanethiol. The redox peaks shift positively in 1M H<sub>2</sub>SO<sub>4</sub>. Furthermore, several small peaks other than the main peak at +580 mV were observed. Thus, the effect of anion on the electrochemical behavior is significant and it seems that the interaction between the anion and the ferrocenium cation formed by oxidation of ferrocene group play very important role in electrochemical response. To make this point clear, we have also investigated the surface structure of the film by FT-IR, XPS and capacitance measurements.



## SECOND HARMONIC GENERATION, A SENSITIVE PROBE OF THE SURFACE ELECTRONIC PROPERTIES OF THE METAL-ELECTROLYTE INTERFACE

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We have carried out systematic absolute measurements of the metal-electrolyte interface non-linearity as a function of the applied potential and analyzed the data by density functional calculations of the non-linear electronic response of charged metal surface in contact with water. By detecting the SH signal of Ag(111)-0.1M KClO<sub>4</sub> solution at various potential values (between -1.35 and .1 V versus SCE), over a wide range of incidence (15-85°) we have identified the non-linear susceptibility component that is sensitive to the induced surface charge. The normal component  $a(\omega)$  of the surface polarization is found to vary by more than one order of magnitude within the range of the applied potential. The important features of the experimental results are well reproduced by the theory : similar overall variation of  $a(\omega)$  which becomes more negative with negative charging, large negative value of  $a$  over most of potential range<sup>(1)</sup>.

Our results demonstrate the usefulness of SHG as a very sensitive probe of the electronic properties of the metal-electronic properties of the metal-electrolyte interface.

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# SPECTROSCOPIC INVESTIGATIONS OF ADSORBATES AT THE METAL ELECTROLYTE INTERFACE USING SUM FREQUENCY GENERATION

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Sum Frequency Generation (SFG) has been already shown to be a unique tool for the vibrational spectroscopy of the liquid-solid interface<sup>(1)</sup>. We present here the first applications to the study of adsorbates, carbon monoxide and cyanide compounds, on noble metal electrodes using a thin layer cell. Carbon monoxide adsorbed from aqueous electrolytes on platinum electrodes is used as a test of the SFG technique since extensive standard IRRAS measurements have been done on this system<sup>(2)</sup>. The SFG signal is very large, leading to a very well defined resonance on a negligible platinum contribution. We observe similar trends as in IRRAS for the frequency shift and oxidation. However the measured potential tuning rate is about a factor of two smaller.

The adsorption of the isoelectronic ion  $\text{CN}^-$  has been on the other hand much less studied. Its smaller IR cross section and the contribution from the ions in solution makes the IRRAS spectroscopy less straightforward<sup>(3)</sup>. Also, SERS is inapplicable to platinum. With SFG, we obtain a very strong contribution from the adsorbed  $\text{CN}^-$ . We observe that  $\text{CN}^-$  adsorption already occurs at -1 V/SCE with a broad band that has a very large potential tuning rate of  $65 \text{ cm}^{-1}/\text{V}$ . Around -0.2 V/SCE a narrower band grows around  $2150 \text{ cm}^{-1}$  with a  $20 \text{ cm}^{-1}$  width and a small potential tuning rate of  $10 \text{ cm}^{-1}/\text{V}$ . As one stays in the double layer potential region, the platinum surface is irreversibly poisoned by the  $\text{CN}^-$ . From a line shape analysis and similar measurements for  $\text{SCN}^-$  adsorption, we propose that the  $\text{CN}^-$  adsorption gives rise to an antiferroelectric bilayer, with the first layer strongly adsorbed through the nitrogen atom. Only the second layer had been already clearly identified<sup>(3)</sup>.

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CONDENSED ORGANIC FILMS AT THE MERCURY ELECTROLYTE INTERFACE  
STUDIED BY SURFACE PLASMON EXCITATION

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In 1958 Lorenz<sup>(1)</sup> reported the first example of a capacitance-potential curve exhibiting a region of constant and strongly depressed interfacial capacitance of an appearance quite distinct from the behavior usually observed with neutral organic adsorbates. Since that time additional examples of such capacitance pits have been observed and attributed to the formation of condensed monolayer films of the adsorbed organic layers<sup>(2)</sup>.

We have investigated the optical properties of this kind of systems using surface plasmon excitation in Attenuated Total Reflection Configuration. We have measured the potential dependence of the Surface Plasmon Resonance for thymine and dansylglycine molecules adsorbed on mercury films electrodeposited onto platinum base<sup>(3)</sup> in contact with NaClO<sub>4</sub> and NaCl supporting electrolytes.

The optical behavior correlates very well with the capacitance behavior. The 2D transition between dilute and condensed adsorbed film is clearly identified during both the anodic and the cathodic potential half-cycles. The influence of various parameters such as the pH, the potential sweep rate, the reactant and anion concentration will be presented and discussed.

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IN-PLANE STRUCTURAL AND ELECTRONIC CHARACTERISTICS OF  
UNDERPOTENTIALLY DEPOSITED COPPER ON GOLD(100) PROBED BY  
IN-SITU X RAY ABSORPTION SPECTROSCOPY

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The process of underpotential deposition (UPD) of submonolayer and monolayer of a metal on a foreign metallic substrate has been intensively studied due to its theoretical interest and its practical importance in many fields such as surface chemistry, electrocrystallization, semiconductor metallization, electrocatalysis. However up to recently, the structure of the electrochemical interface has been described only indirectly using optical and ex-situ measurements. There is the question in ex-situ studies whether the structure and oxidation state of the compound has changed upon removing it from the electrolyte and the potential control.

In this view, X ray Absorption Spectroscopy (XAS) appears well adapted to get in-situ electronic and structural informations of the UPD layer. In-situ XAS spectra of electrochemically deposited monolayer and bilayer of copper on a gold (100) surface immersed in an electrolytic solution and under potential control were obtained by using fluorescence detection under grazing incidence, the X rays being polarized parallel to the plane of the gold surface.

For a full-coverage monolayer of copper, the X ray Absorption Near Edge Structure (XANES) clearly revealed that a charge transfer process occurred from the copper atoms to the gold substrate where the oxidation state of copper was closed to  $Cu^{1+}$ . The nearest neighbors were determined to be oxygen at  $1.97 \pm 0.03 \text{ \AA}$  and copper at  $2.66 \pm 0.03 \text{ \AA}$ . The copper-copper distance lies in between the gold-gold lattice spacing ( $2.88 \text{ \AA}$ ) and the copper-copper one ( $2.54 \text{ \AA}$ ) which seems to indicate that a structural rearrangement of the first gold atom layer occurs. The observation of copper backscattering only suggests the copper atoms sit in an "atop" site. This geometry associated to the charge transfer process is stabilized by oxygen atoms coming from the water molecules or from the sulfate ions.

When two copper layers were electrochemically deposited on gold (100), strong structural modifications were observed. No oxygen is detected and the near neighbors correspond to copper at  $2.59 \pm 0.03 \text{ \AA}$  and copper at  $2.90 \pm 0.03 \text{ \AA}$ . The second copper-copper distance is very close to the usual gold-gold lattice spacing suggesting that the first copper layer forms a commensurate phase on the gold (100) surface. The first distance due to second copper layer is close to the copper-copper lattice spacing but a small mismatch is still observed. These results reveal that a reconstruction process occurs when one copper layer is added onto the first one where the copper atoms evolve from an "atop" site stabilized by oxygen to a 4 fold hollow site.

## NEW EXPERIMENTAL DATA FOR THEORY

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This lecture will scrutinize some recent experimental data which can help to gain insight into the structure of the electrode/electrolyte interface, and can inspire theorists to better model the boundary region. Since in situ measurements using "non-traditional" techniques will be discussed in another session, this lecture will be devoted to the analysis of recently measured "traditional" parameters, such as zero charge potential, differential capacitance, their temperature coefficients, Volta potential difference.

The major part of the "classical" experimental work carried out in the past few years has concerned the polycrystalline and monocrystalline Bi electrode in aqueous and non-aqueous solvents, as well as single crystal faces of Ag and Au. For the last two metals the effect of temperature has also been investigated. While the general picture has not changed substantially for the sp-metals during the past decade, a major issue remains the interpretation of the behaviour of Ag and Au (and Cu). If the data for these metals are analyzed in the context of all others, their position turns out to be totally anomalous. It is thought that this may be related to the higher polarizability of the electron tail at the surface of sd-metals. Results point out that the metal-water interaction is probably weak while electric effects related to such interaction are outstanding.

Experiments show that the accuracy obtainable with liquid electrodes (Hg, Ga, In-Ga) is still not achievable with sd-metals, despite the outstanding progress made recently. The characterization of the structure of metal single crystal faces and the reproducibility of data obtained in different laboratories can still be improved considering that some contrasting features are observed which render any interpretation somewhat ambiguous. These include (i) the dependence of the potential of zero charge on the work function of the metal crystal face and on the nature of the electrolyte, (ii) the variation of the inner layer capacitance with the crystallographic orientation, and (iii) the temperature coefficient of the potential of zero charge. This particular situation may well be related to the way the electrode surface is prepared for the measurements. No general consensus has thus far been reached on the interpretation of the experimental picture, especially as far as the nature of the metal-solvent interaction is concerned.

Even in the case of liquid Hg, a debate is still open concerning the value of the Volta potential difference for the uncharged metal surface in water. Two groups of data are presently available differing by as much as 0.3 V. The implications in terms of double layer structure will be scrutinized considering alternatively each group of data as the most reliable. Such an analysis will enable to show that only one of the two values gives a realistic picture in the light of our present understanding.

# Application of Scanning Tunneling Microscopy (STM) to Semiconductor/Electrolyte Interfaces

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Scanning tunneling microscopy (STM) has been proved to be very useful in observing morphology of metal electrode surfaces in solution. STM has been also applied to monitor the surface structure of semiconductor electrodes. There exists, however, some difficulty when STM is applied to semiconductor/electrolyte interfaces. When the potential of n-type (p-type) semiconductor is more positive (negative) than the flat band potential, the depletion region is formed within the semiconductor and the tunneling is impeded. In other words, one should be able to probe the electronic characteristics of semiconductor/electrolyte interfaces by monitoring the tip current as a function of the potential of the semiconductor electrode.

We used n-GaAs and p-GaP single crystal as electrode and measured the tip current as a function of the potential of the semiconductor electrode. It was found that the tunneling is possible as far as the semiconductor is in accumulation in all the cases we investigated. When the carrier density of the semiconductor is low, as soon as depletion layer is formed the pre-set tunneling current is not attained anymore and the tip crashes onto the surface. On the other hand, when the carrier density is high, the tunneling mode is maintained even when the semiconductor is in weak depletion. The tip crashes onto the surface if the depletion layer becomes thicker and the contact current flows between the tip and the semiconductor. The tunneling mode was retained again under strong depletion (inversion) condition. The effect of the tip potential on the critical potential at which the tunneling mode becomes contact mode was also investigated. Surface structures of the semiconductors were studied under various bias conditions.

# Charge Transfer Reaction Inverse Photoemission Spectroscopy (CTRIPS) at Gold/Acetonitrile Solution Interface

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The information of electronic states of electrodes, e.g., metals and semiconductors, is very important to understand how electrochemical reactions proceed at electrode/electrolyte interfaces. Charge transfer reaction inverse photoemission spectroscopy (CTRIPS) originally proposed McIntyre and Saas(1) seems to be a very useful technique to probe both unoccupied and occupied electronic states of electrodes in solution, although the quantitative interpretation of the observed spectrum is rather difficult.

In this work, we have studied CTRIPS at gold electrode in acetonitrile solution containing one of three redox species (benzophenone, t-stilbene and benzonitrile).

In CTRIPS measurement, the electrode potential is stepped first to a negative potential where the anion radical of the species is generated and then to various positive potentials ( $U_f = -0.5 \sim 0.7\text{V vs. Ag/Ag}^+$ ) where the anion radical is oxidized. Light is observed while the electrode is kept at  $U_f$ . High energy threshold of CTRIPS spectrum,  $E_{th}$ , decreases linearly as the potential of gold electrode becomes more negative, confirming the emission is due to CTRIP process. The energy of injected electron,  $E_{inj}$ , with respect to the Fermi level may be represented by the difference between the redox potential of the species,  $U^0$ , and  $U_f$  ( $E_{inj}/e = -(U^0 - U_f)$ ). If the relaxation is solely to the bulk unoccupied states, not only  $(E_{th} - E_{inj})$  but also the shape of the spectrum should be independent of  $U_f$ . The peak position with respect to  $E_{th}$ , however, varies with electrode potential and is not affected by the redox potential of the electron injection species at a given electrode potential. The emission efficiency also depends on the potential. From these results, we proposed that the emission is due to charge transfer reaction inverse photoemission (CTRIP) process which takes place via surface state.

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A reappraisal of the frequency dependence of the impedance of semiconductor electrodes.

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During the last three decades the impedance of polarizable semiconductor/metal contacts has been studied intensively. In contrast to the predictions of the Mott-Schottky theory it is clear that the capacitance of the semiconductor electrode under depletion conditions generally depends on the frequency  $\omega$  of the perturbation signal. Different theories have been proposed to explain the anomalous frequency dependence. This dependence is generally attributed to chemical and/or structural faults within the solid (1,2).

We reinvestigated the problem making use of various n-GaAs/electrolyte and n-GaAs/Au contacts (single crystal GaAs (100)-face). Our results can be summarized as follows:

1. The impedance of the GaAs electrodes can be described as a constant phase element:  $Z = A (i\omega)^{-n}$  with  $1 > n > 0$ . As in most cases  $n > 0.9$ , it is convenient to investigate in detail the frequency dependence of the series capacitance  $C_s$ .
2. At a given GaAs/electrolyte contact  $C_s$  decreases almost linearly with  $\log \omega$  ( $n < 1$ ). At a GaAs/Au contact  $C_s$  is nearly independent of  $\omega$  ( $n \approx 1$ ).
3. At a given frequency,  $C_s$  increases with the specific conductivity  $\kappa$  of the electrolyte.
4. Points 2 and 3 are interrelated: a pronounced  $\omega$ -dependence at a given  $\kappa$  corresponds to a pronounced  $\kappa$ -dependence at a given  $\omega$ .
5. The dependence of  $C_s$  on  $\omega$  (and  $\kappa$ ) is related to the pretreatment of the GaAs-electrode. It appears that  $C_s$  measured at mechano-chemically polished GaAs electrodes shows a less pronounced  $\omega$ -dependence than at electrodes which were subjected to anodic dissolution at high band-bending.

The observations 2-5 on GaAs semiconductor electrodes are very similar to those of Scheider (3) and many other authors on polarizable metal electrodes. We therefore believe that the  $\omega$ -dependence of the polarisation capacitance of semiconductor and metal electrodes has a common origin. The fact that this  $\omega$ -dependence is more pronounced at electrodes with a microscopically rougher surface suggests that the  $\kappa$ - and  $\omega$ -dependence of the impedance is due to inhomogeneous distribution of current and potential at the electrode/electrolyte interface.

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## ELECTROLYTES IN MICROPORES

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The ability of porous materials to exclude electrolyte forms the basis of important technological processes for the desalination of water. The experimental data show that  $\text{Na}_2\text{SO}_4$  solution, which contains the divalent coion (ion having the charge of the same sign as the surface charge) is rejected more strongly than  $\text{NaCl}$  at the same sodium concentration. Further, for  $\text{NaCl}$  solution the rejection decreases by increasing the salt concentration (at fixed surface charge density), and increases by increasing the surface charge. The geometry and size of the micropores may play an important role as well; narrow pores are more efficient in excluding the electrolytes. In this work we will show that many of these findings can be understood by using the simple model of cylindrical capillary system and the Poisson-Boltzmann theory of the electrical double-layer.

Some experimental evidence suggests that the phenomenon is more complicated if multiply charged ions are present in the solution [1]. Surprisingly, the exact opposite effect, namely the enrichment of electrolyte was found in systems containing multivalent counterions ( $\text{MgCl}_2$ ). This result cannot be understood on the basis of the electrostatic theories and it is assumed that specific interactions take place. The computer simulation data obtained recently [2] offer another explanation for this effect. With multivalent counterions and at higher charge densities, the correlations between ions in the electrical double-layer may be so strong as to cause the "charge inversion" [3], and the anomalous behavior mentioned above.

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# Electric Double Layer Structure at the Dielectric/Solution Interface

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Electrical phenomena at a dielectric/solution interface attract a steady attention in view of their fundamental importance in problems of physical and colloid chemistry, electrochemistry, biophysics and bioelectrochemistry. Systems of this type include various contacts of an electrolyte solution with surfaces of solid dielectrics, colloid particles, biological and polymer membranes, oxide film covered electrodes as well as some boundaries of two immiscible liquids.

Description of their interfacial structures, adsorption and electrokinetic phenomena, energetics of solid dielectrics interaction via a solution is usually carried out within the framework of the Stern concept. Distributions of the electric potential and ionic concentrations are considered within the Gouy-Chapman theory, the source of the field (charges of the dielectric surface layer) is "smeared out" uniformly along the boundary, and the Langmuir isotherm is used for the equilibrium between adsorption centers and the solution surface layer.

Two essential factors are not incorporated in such treatment, namely:

discreteness-of-charge effects due to non-uniformity of the surface charge distribution along the interface as well as its redistribution in the course of an additional species adsorption;

effects of a spatial structure of the media in contact and of the interfacial region which manifest themselves in electric phenomena by means of a nonlocal coupling (via an integral relation) between the spatial distributions of the polarization and the total electric field.

This report is an overview of the results obtained by our group<sup>1</sup> concerning the influence of both these factors.

A consistent theory of the above phenomena must be based on a detailed analysis of interaction energies of individual ions and surface groups both between each other and with the interphase. We have found that both interaction potentials, ion-interphase and ion-charged surface group, within the solution region near the dielectric edge deviate drastically from the results of the traditional theory - real interaction energies may be 10-20 times larger. An attraction region for a solute ion near an uncharged surface is predicted for a not very low value of the dielectric constant of the medium in contact. The shift of dissociation or binding constants for surface ionogenic groups, in comparison with those in the bulk solution, is found. Long-range interactions between ions and/or charged groups within the interfacial layer turned out to be determined by two additive contributions, due to interaction via the solution and the dielectric. This interaction energy,  $U$ , is decreasing as  $R^{-1}$  within a wide range of the distances between the species,  $R$ . With using these results a statistical-mechanical theory has been proposed for thermodynamic and correlation characteristics of two-dimensional ensembles of discrete charged species within the interphase. A "Coulomb-like" behavior of the binary interaction potential,  $U \sim R^{-1}$ , at intermediate distances between the species results in a complicated variety of the correlation properties of the ensemble depending on the total charge density, in particular plasma-type phenomena. Simple analytical expressions have been derived for characteristics of adsorption equilibrium. Conditions are formulated when account for discreteness-of-charge effects is of crucial importance.

Electric double layer structure in an electrolyte solution of a medium concentration has been studied. A nonlocality of the solvent polarization response is revealed to result in a considerable deviation of ionic concentration and potential distributions from the Gouy-Chapman ones if the ionic strength of a 1-1 aqueous electrolyte exceeds 0.1M. The sign of this deviation may depend on the energetic characteristics of an individual ion interaction with the boundary, i.e., on the difference of the closest approach planes for the solvent and ions. The conclusion has been drawn for this concentration range that the proximity of the total potential drop (or the interfacial capacitance) to the results of the traditional theory does not mean that this simplified approximation is adequate with respect to the potential or ionic concentration profile within the layer. The spatial solvent structure leads to a very slow decrease of the induced ionic charge far from the boundary, its decrement being determined by the parameters of solvent polarization correlations

(instead of the Debye screening length) and being about  $10\text{\AA}$  for aqueous solutions. Some expectations concerning nonlocality effects in the electrokinetic phenomena as well as in energetics of interaction between the solid surfaces via an electrolyte solution are discussed.

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# **In-situ X-ray Reflectivity and Diffraction Studies of the Au(001) Reconstruction in an Electrochemical Cell**

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In-situ x-ray specular reflectivity and glancing incident angle x-ray diffraction measurements have been performed at the Au(001) surface in a 0.01M  $\text{HClO}_4$  solution under controlled potentials in an electrochemical cell. The gold single crystals are mechanically polished, electropolished, sputtered with  $\text{Ar}^+$  ions and annealed at  $700^\circ \text{C}$  in vacuum. After cooling to room temperature the crystal is transferred through air to the in-situ x-ray electrochemical cell and immersed in the solution at -0.3 volts referenced to a Ag/AgCl(3 M KCl) electrode.

As transferred at -0.3 volts, the in-plane x-ray diffraction pattern is consistent with the "5x20" hexagonal surface structure as observed in vacuum. At potentials above 0.6 volts the hexagonal diffraction spots rapidly disappear and the diffraction pattern exhibits a "1x1" structure. The hexagonal reconstruction almost fully recovers at negative potentials after several hours. Initially after immersion the hexagonal diffraction spots are aligned along the (110) and ( $\bar{1}\bar{1}0$ ) directions. The diffraction pattern from subsequent potential cycles exhibits domains rotated by  $0.8^\circ$  from these cubic directions.

Absolute specular reflectivity (00L) profiles were measured in both the reconstructed and nonreconstructed potential ranges. The reflectivity data has been fit to a simple real space model where each atomic layer is specified by a mass density, a surface normal expansion coefficient, and a Gaussian roughness (surface Debye Waller factor). Excellent fits are obtained by adjusting the density and expansion of the top layer and the Gaussian roughness for the top layer and several subsequent layers. The reconstructed overlayer has a mass density which is 121% of a normal bulk (001) layer and which is expanded in the surface normal direction by 20% relative to the bulk layer spacing. These results are in close agreement with the vacuum observations. At potentials above 0.6 volts, a new layer with a density of only 22% of a bulk layer is formed. This indicates clearly that the extra atoms popped up from the dense hexagonal overlayer do not segregate to the kink sites. From the coherence area of the scattering experiments we presume that these new layer consists of small clusters or isolated atoms. The existence of this low density top layer and the reversibility of the transition are believed to play an important role in the electrochemical studies on gold single crystal electrodes. Further studies are continuing.

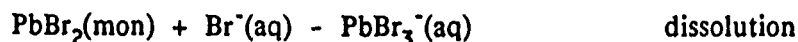
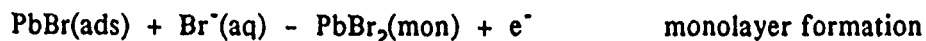
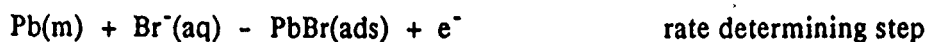
# MONOLAYER DEPOSITION OF LEAD BROMIDE ON THE LEAD ANODE: KINETICS AND ENERGETICS

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When lead is anodised in aqueous electrolytes containing bromide a porous film of lead bromide forms, commencing at the equilibrium potential (  $-285$  mV SHE at  $1$  mol/L  $\text{Br}^-$  ). Some dissolution also takes place, giving complexes of the type  $\text{PbBr}_4^{2-}$ . It was found that film formation is preceded by the appearance of a monolayer at an underpotential of  $-25$  mV with respect to the equilibrium potential for crystalline lead bromide. In potential sweep experiments, the monolayer was detected as a small anodic peak, with a peak current density proportional to the potential sweep rate. The corresponding cathodic peak was also proportional to the potential sweep rate, with a charge density of  $670 \mu\text{C cm}^{-2}$ . This is consistent with a monolayer of  $\text{PbBr}_2$  on an electrode with a measured roughness factor of 4, given that the 100 plane of the lead bromide crystal corresponds to a calculated charge density of  $167 \mu\text{C cm}^{-2}$ .

Potential step transients revealed that the monolayer forms by direct chemisorption onto surface sites at a rate proportional to the fraction of unoccupied surface sites ( $1 - \theta$ ). Simultaneous dissolution also takes place to give bromo-complexes, as show by the effect of stirring. The data fit the following mechanism.



In the case of lead iodide, a reversible monolayer was observed [1], while the lead chloride system shows no detectable monolayer [2], probably because the competing dissolution is dominant.

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## Redox Properties of $\text{WO}_3$ -incorporated Polypyrrole Films

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This paper describes electrochemical synthesis and redox properties of  $\text{WO}_3$ -incorporated polypyrrole (PPy) films. As reported previously [1], the oxide incorporation of pyrrole in the presence of suspended oxides occurs for oxides having the isoelectric point lower than pH ca 4 such as  $\text{WO}_3$  and  $\text{SiO}_2$  provided that the solution pH is high enough to build up negative charges on the oxide surfaces. Aqueous 0.1 M pyrrole containing suspended  $\text{WO}_3$  meets such requirement without using any electrolyte. The resulting  $\text{WO}_3$ -incorporated PPy films show redox activities in aqueous acidic KCl solutions. The incorporated  $\text{WO}_3$  serves not only as the fixed dopant but also as an electrochemically active substance to give hydrogen tungsten bronze. During the redox reaction of  $\text{WO}_3$ -incorporated PPy, the doping and undoping of electrolyte cations ( $\text{K}^+$  ions) as well as the bronze formation occur.

The  $\text{WO}_3$  incorporation can be reduced by adding appropriate electrolyte anions such as  $\text{ClO}_4^-$  to the deposition baths. By changing the amount of  $\text{ClO}_4^-$  in the PPy deposition baths with fixing the amount of  $\text{WO}_3$ , PPy films of a variety of  $\text{WO}_3/\text{ClO}_4^-$  ratios can be prepared. The resulting PPy exhibits redox activities with involvement of both electrolyte cations and anions of the electrolyte solution in which the PPy is immersed. Photo-sensitivities and electrochromic properties of the resulting PPy films are greatly influenced by the ratio of doped  $\text{WO}_3$  to  $\text{ClO}_4^-$ .

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DYNAMIC METHODS IN IN-SITU FT-IR REFLECTION  
SPECTROELECTROCHEMICAL STUDIES

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It is important to set up methods to monitor the time-resolved spectra of reactive species in in-situ FT-IR reflection spectroelectrochemical studies. In this paper, we report some results about the time-resolved spectra of the oxidation process of  $\text{Fe}(\text{CN})_6^{4-}$  on platinum electrode and glassy carbon electrodes which have different surface states. We also presented results about the oxidation process of glassy carbon electrode which is relate to the "electrochemical pretreatment". Results showed the time-dependence of  $\text{Fe}(\text{CN})_6^{4-}$  oxidized on platinum electrode is diffusion-controlled. On the different surface state of GCE, the oxidation behaviour of  $\text{Fe}(\text{CN})_6^{4-}$  is different. i.e. changes of spectra on pretreated GCE is slow than that of unpretreated GCE, the potential difference is as high as 300mv. The cause of these phenomena is not clear, it may be ascribed to the effect of different oxide group and different morphology on the surface. Combined with the time-resolved spectra and LSPIRS (linear scan potential infrared spectroscopy) of oxidation process for GCE, we suggested that oxidation way should be: a. activation of graphite ring. b. opening ring (i.e. producing acid anhydried).